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Environmental Assessment Data Base for Petroleum Refining Wastewaters and Residuals

Tulsa Univ., OK

Prepared for

Robert S. Kerr Environmental Research Lab.
Ada, OK

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ENVIRONMENTAL ASSESSMENT DATA BASE FOR PETROLEUM REFINING WASTEWATERS AND RESIDUALS

by

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EPA Grant No. R 805099

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The objectives of this project were to develop an environmental assessment data base for characterizing and treatment of petroleum refinery wastewaters and residual sludges, and recommendation of further research needed to improve the data base.

The project was conducted in three phases. Phase 1 was the establishment of a Peer-Group Review Committee to provide direction to the project and to ensure that a diversity of viewpoints was considered. Six eminent experts in the waste treatment field were chosen to serve on the committee.

Phase 2 involved the preparation of four comprehensive state-of-the-art reviews, by outside consultants, to provide the environmental assessment data base on refinery wastewaters and residual sludges.

Phase 3 included a critical examination of the four individual state-of-the-art reviews, selection of eight areas where further research was considered to be needed to improve the data base, and preparation of this report.

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FOREWORD

The Environmental Protection Agency is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise, and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life. In partial response to these mandates, the Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma, is charged with the mission to manage research programs to investigate the nature, transport, fate, and management of pollutants in ground water and to develop and demonstrate technologies for treating wastewaters with soils and other natural systems; for controlling pollution from irrigated crop and animal production agricultural activities; for developing and demonstrating cost-effective land treatment systems for the environmentally safe disposal of solid and hazardous wastes.

In a coordinated research effort with the industrial and the academic communities, the EPA has generated a large data base from the application of treatment and control technologies to petroleum refinery wastewater and residuals. This report summarizes the available information as a function of specific technologies and projects the remaining research needs.

Clinton W. Hall

Clinton W. Hall, Director
Robert S. Kerr Environmental
Research Laboratory

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This report was submitted in fulfillment of Contract R805099010 by the University of Tulsa under sponsorship of the U. S. Environmental Protection Agency. The report covers the period from June 1978 to June 1981, and work was completed as of June 1981.

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LIST OF ABBREVIATIONS

AC	-- activated carbon
API	-- American Petroleum Institute
AS	-- activated sludge
BAT	-- best available pollution control technology
BCT	-- best conventional pollution control technology
BMP's	-- best management practices
BOD	-- biological oxygen demand
BPCTCA	-- best practicable control technology currently available
BPT	-- best practical pollution control technology
BTX	-- benzene, toluene, xylenes
CAM	-- carbon adsorption method
COD	-- chemical oxygen demand
CPI	-- corrugated plate interceptor
DAF	-- dissolved air flotation
DEA	-- diethanol amine
DOE	-- Department of Energy
EPA	-- Environmental Protection Agency
ES	-- Engineering-Science, Inc.
FC	-- final clarifier
FCC	-- fluid catalytic cracking
GAC	-- granular activated carbon
GC	-- gas chromatograph
GLC	-- gas liquid chromatography
IAF	-- induced air flotation
IR	-- infrared
LPG	-- liquefied petroleum gas
MEK	-- methyl ethyl ketone
MIBK	-- methyl isobutyl ketone
MLVSS	-- mixed liquor volatile suspended solids
MMF/AC	-- mixed media filter/activated carbon
MS	-- mass spectrometer
NMP	-- n-methyl-2-pyrrolidone
NSPS	-- New Source Performance Standards
PAC	-- powdered activated carbon
PONA	-- paraffin-olefin-naphthene aromatic
POTW	-- Publicly Owned Treatment Works
PPI	-- parallel-plate interceptor
p.t.b.	-- pounds per thousand barrels
RBS	-- rotating biological surface
RCRA	-- Resource Conservation and Recovery Act
SDA	-- solvent de-asphalting
SPCC	-- spill prevention and countermeasure
TDS	-- total dissolved solids
TOC	-- total organic carbon
TOD	-- total oxygen demand
TON	-- threshold odor number
TSS	-- total suspended solids

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SECTION 1

INTRODUCTION

The goals of the present work were to develop a complete environmental assessment data base concerning the treatment of petroleum refining wastewaters and residuals, and the recommendation of areas where further research is needed to improve the data base. The goals were achieved by establishing a Peer-Group Review Committee, developing state-of-the-art reviews by outside consultants, compilation of the sate-of-the-art reviews, and selection of those areas where further research could be most useful.

A Peer-Group Review Committee of six people, chosen for their expertise in refinery wastewater treatment, was selected by the Project Manager in consultation with the Project Officer and the Robert S. Kerr Environmental Research Laboratory. The committee provided oversight direction to the project and included acknowledged experts, most of whom had actual experience in petroleum refinery wastewater management. The members of the committee were chosen so as to represent a broad spectrum of diverse viewpoints from industry, universities, the American Petroleum Institute (API) and the consulting field.

To develop the environmental assessment data base, state-of-the-art reviews were prepared on these four topics:

1. Characterization of the petroleum refining industry and refinery wastewaters. The parameters affecting the generation of wastewater pollutants are discussed, including crude oil compositions, refinery technologies and classifications, wastewater sources and their pollutants. Future trends for the refining industry are included.

2. A pollutant discussion and rationale for characterizing the wastewaters from petroleum refining and their toxicity effects upon aquatic organisms. This rationale includes a review of the analytical procedures used to measure, define and assess the effects of the various pollutants. The list of pollutants considered includes the current permit parameters (chemical oxygen demand, COD; biological oxygen demand, BOD; etc.) as well as the priority pollutants.

3. A comprehensive discussion and evaluation of existing and emerging wastewater treatment and control technology. Data on the performance capabilities of the various technologies are included.

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4. A compilation of data on the discharge levels of refinery wastewater pollutants including their avenues of discharge. The data include estimates of accuracy, precision, variance and causes of variance whenever possible.

Based upon a critical examination of the individual state-of-the-art reviews, areas within the existing data base were selected as meriting further research to improve the environmental assessment data base. Each of the specific areas selected are discussed so as to explain why further research might be fruitful and to highlight the benefits that might be expected of such research. The recommended research needs are summarized in the Conclusions and Recommendations section of this report.

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SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Existing refinery technology is very complex and the development of new technology is an on-going process. Within the 20-year period of 1940-1960, a number of technological "breakthroughs" occurred which included the development of fluid catalytic cracking and processes involving catalysis in a hydrogen atmosphere (catalytic reforming, hydrotreating and hydrocracking). With the current body of knowledge on catalytic processes, the future development of new refinery technology is expected to be more evolutionary in nature. Another period of rapid technological breakthrough is not expected.

Many refineries already practice the in-plant reuse of treated wastewaters to some extent and air-cooling has replaced much water-cooling. There is little likelihood that more intensive emphasis on wastewater reuse will dramatically reduce wastewater volumes.

In general, the current technology for refinery wastewater treating (consisting of in-plant reduction of wastewater generation, primary removal of oil and suspended solids, and secondary treatment via biological oxidation) can satisfy the regulatory criteria for control of the conventional pollutants such as oil, suspended solids, BOD, COD, phenols, sulfides, ammonia, etc. There is much evidence that the current wastewater treatment technology essentially removes or degrades those pollutants which cause lethal, short-term toxicity to fish.

Eight areas have been identified in which further research is needed to improve the environmental assessment data base for characterizing and treating refinery wastewaters and residual sludges. Those areas of research needs are briefly listed below:

ACTUAL PLANT DATA COLLECTION AND CORRELATION

1. Correlation of the key design factors in activated sludge biotreatment, such as mixing horsepower and reaction basin retention time, with pollutant removal efficiency.
2. Correlation of actual case history data on the use and effectiveness of chemical oxidants (hydrogen peroxide, chlorine and ozone) in treating refinery wastewaters.

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LABORATORY-SCALE RESEARCH AND DEVELOPMENT

3. Identifying which specific refinery wastewater pollutants exhibit long-term fish toxicity (lethal or sub-lethal). Development of techniques for the rapid determination of long-term fish toxicity.

4. Determination of which analytical test methods are the least reliable and their contribution to overall effluent quality variability. Development of new, more reliable test methods, if possible.

PILOT-AND DEMONSTRATION-SCALE RESEARCH

5. Development of an economic method for recoverying and regenerating the spent powdered activated carbon (PAC) used to enhance the performance of activated sludge biotreaters.

6. Funding the demonstration and operation of the granular activated carbon (GAC) process (for the tertiary treatment or secondary treatment of refinery wastewaters[a]) in a unit capable of treatment of 200-400 gpm of refinery wastewater.

7. For the landfarming of oily sludges, determination of the relationship between sludge vapor pressure and problems of odor control and air emissions. Develop methods for mitigating such problems. Also investigate methods of resolving problems with landfarming vis-a-vis Resource Conservation and Recovery Act (RCRA) regulations if such problems exist.

FEASIBILITY AND GUIDANCE STUDY

8. Development of a comprehensive feasibility and guidance study regarding the methods of producing a concentrated, residual pollutant brine (reverse osmosis and evaporation) and the ultimate disposal of residual wastewater pollutants in evaporation-percolation ponds, subsurface injection wells and remote disposal dumps. Such a study should include a realistic assessment of capital costs and energy usages as well as a realistic assessment of the benefits to be expected in terms of the magnitude of improvement in the quality of the nation's waters. The study should also assess the cost-benefit ratio of the Environmental Protection Agency's (EPA) New Source Performance Standards (NSPS) "no discharge" requirement for refineries relative to control of other pollutant sources such as non-point sources.

The above order of listing for the recommended research needs is not intended to be a prioritized listing. The listing is merely categorized so as to present the least costly

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[a] A description of the successful use of the GAC process for the secondary treatment of wastewater in a Japanese refinery (on a full-plant scale) has been published in the Oil & Gas Journal of May 11, 1981.

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research recommendations first and the most costly recommendations last. A more detailed rationale for the recommended research needs is presented in Section 9 of this report.

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SECTION 3

CHARACTERIZATION OF PETROLEUM REFINING INDUSTRY AND PETROLEUM REFINERY WASTEWATERS

M. R. Beychok
Environmental Consultant
California

INTRODUCTION

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Most petroleum refineries are similar in that they process a crude oil raw material so as to produce a variety of endproducts. But beyond that similarity, the refining industry encompasses a broad range of refinery types consisting of an even broader range of refining technologies or unit processes and producing a wide spectrum of motor gasolines, heating and industrial fuel oils, lubricating oils and petrochemicals. The purpose of this section is to provide a brief discussion and explanation of petroleum refineries and the unit processes involved in the design and operation of refineries.

TYPES OF REFINERIES

Refineries differ considerably in terms of their range of endproducts. Some refineries maximize the production of motor gasolines and some maximize the production of heating oils and industrial fuel oils. Other refineries emphasize the production of lubricating oils, and still others are designed to produce petrochemical endproducts or intermediate products for sale as feedstocks to petrochemical plants.

In some cases, refineries shift their endproduct emphasis on a seasonal basis. For example, motor gasoline production will be maximized for the spring and summer, and heating and fuel oil production will be maximized for the fall and winter.

Many so-called combination refineries produce a product slate (endproduct range) that includes the entire spectrum of gasolines, heating oils, industrial fuels, lubricating oils and petrochemicals.

In general, most petroleum refineries can be categorized as being within one or more of the following types in terms of their product slate:

- Motor gasoline refineries

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- Heating and fuel oil refineries
- Lubricating oil refineries
- Petrochemical refineries
- Combination refineries

As will be discussed later herein, in terms of wastewater generation and composition, refineries are probably better categorized by their complexity as defined by the types of unit processes or technologies used within the refineries.

THE COMPOSITION OF PETROLEUM CRUDE OIL

The key factors involved in selecting the unit processes or technologies used within a petroleum refinery are the desired product slate and the composition of the refinery's raw material crude oils. Since the amount and composition of wastewaters generated by a refinery are largely dependent upon the processes used in the refinery, it becomes evident that the composition of the raw material crude oils is one of the factors which determines the generation and composition of refinery wastewaters. Thus, it is important to have some understanding of the nature of petroleum crude oils and, in particular, to understand that crude oils obtained from different geographic oil field sources can and do have significantly different compositions.

Petroleum crude oil is primarily a mixture of various "hydrocarbons", which are chemical molecules composed of hydrogen and carbon atoms. Those molecules may be quite simple or quite complex in the structural arrangement or linking of their component atoms. The carbon atoms may be linked together in short or long straight chains with or without branched "side-chains", or they may be linked together in cyclic or ring arrangements. The simpler hydrocarbons found in crude oils are "paraffins" or "saturated hydrocarbons" in which each carbon atom is linked with the maximum possible number of hydrogen atoms in accordance with the generic formula of C_nH_{2n+2}. For example, a paraffin molecule with 10 atoms of carbon (C) would be linked with 22 atoms of hydrogen (H). The saturated or paraffinic hydrocarbons may be "normal" paraffins in which carbon atoms are linked in straight chains, or "isoparaffins" in which the carbon atom linkage includes branched chains. For example, normal pentane which is n-C_5H_{12} and isopentane which is i-C_5H_{12} both have the same number of carbon and hydrogen atoms in accordance with the generic paraffin formula of C_nH_{2n+2}, but normal pentane has five carbon atoms in a straight chain while isopentane has a branched linkage of five carbon atoms.

Hydrocarbons with straight or branched carbon atom chains and containing less than the maximum of four hydrogen atoms per carbon atom are called "unsaturated" or "olefinic". For example, pentene (C_5H_{10}) is unsaturated or mono-olefinic, and pentadiene (C_5H_8) is even more unsaturated or di-olefinic.

The carbon atoms in hydrocarbon molecules may also be linked together to form closed cycles or rings. When the carbon atoms in cyclic hydrocarbons are linked to the maximum number of hydrogen atoms possible for such cyclic arrangements, the molecules

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are "saturated naphthenic hydrocarbons" with the generic formula of C_nH_{2n} (which is the same as for the unsaturated mono-olefins discussed above). The naphthenic hydrocarbons are usually named with the prefix of "cyclo", as in cyclo-pentane (C_5H_{10}). Naphthenic hydrocarbons may also be unsaturated as in cyclo-pentene (C_5H_8).

When hydrocarbon molecules have six carbon atoms linked together in a ring containing three unsaturated links, the molecules are called aromatics. For example, benzene is an aromatic with the formula of C_6H_6. The aromatic ring may also be linked to a saturated side-chain as in toluene (C_7H_8) and xylene (C_8H_{10}) or to an unsaturated side-chain as in styrene (C_8H_8), all of which fall within the category of aromatics.

Petroleum crude oils contain literally hundreds of different hydrocarbons, many of which are very much more complex in their molecular structure than those discussed above. However, the analysis of a crude oil in terms of the relative quantities of the four molecular categories discussed above provides a valuable insight as to the unit processes that will be required in a refinery designed to produce a specific product slate from that crude oil. Such analyses are called PONA's which is an acronym for paraffin-olefin-naphthene-aromatic analyses[a].

Crude oils also contain various amounts of organic sulfur and organic nitrogen compounds. Some of the unit processes used in many refineries are designed to catalytically "desulfurize" certain of the intermediate products within the refinery. Those desulfurization processes convert organic sulfur and nitrogen into gaseous hydrogen sulfide (H_2S) and ammonia (NH_3) which are then removed in large part by stripping or distillation. However, a small part of the H_2S and NH_3 almost invariably appears in some of the refinery wastewaters in the form of ammonium hydrosulfide (NH_4SH) in amounts ranging from about 100 ppm to 10,000 ppm or more[1]. Refinery wastewaters containing ammonium hydrosulfide or free hydrogen sulfide are commonly referred to as "sour waters" which may also be generated from unit processes other than catalytic desulfurizers. The amount of hydrogen sulfide and ammonia contained in refinery sour waters (as NH_4SH) is directly related to the organic sulfur and organic nitrogen contents of the raw material crude oils as well as to the type of unit processes used in a specific refinery.

As discussed above, all crude oils are a complex mixture of hydrocarbons. However, the amount of "light" or low-boiling hydrocarbons relative to "heavy" or high-boiling hydrocarbons varies very considerably from crude oil to crude oil. In very generalized terms, the hydrocarbons in crude oil can be classified by their boiling range and number of carbon atoms. Starting with the lightest or lowest-boiling hydrocarbons (which are gases) and proceeding up the boiling range scale to the heavy fuel oils, yields:

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[a] Crude oils rarely contain any olefinic hydrocarbons. However, olefins are produced by subsequent refinery processing.

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	Number of carbon atoms	Atmospheric boiling range (°F)
Methane, ethane (gases)	1,2	-259, -128
Propane, butane	3,4	-44, 31
Naphthas (gasolines)	5 to 11	100 to 400 [a]
Diesel and heating oils	10 to 15	350 to 600 [a]
Industrial fuel oils	16 plus	600 plus

[a] Designates range of initial boiling point to final boiling point.

Crude oils such as those from Qatar in the Middle East with a specific gravity of 0.82 (an API gravity of 41°) and containing about 38 volume percent of naphthas are referred to as "light" crude oils because of their relatively low specific gravity and relatively high content of hydrocarbons in the naphtha boiling range of 100 to 400 °F.

Crude oils such as those from Bachaquero in South America with a specific gravity of 0.95 (an API gravity of 17°) and containing about 10 volume percent of naphthas are referred to as "heavy" crude oils because of their relatively high specific gravity and relatively low content of hydrocarbons in the naphtha boiling range.

The amounts of the various boiling range materials in a crude oil and the physical properties of the individual boiling range materials (specific gravity, sulfur and nitrogen contents, PONA analyses, etc.) are determined by a complete crude oil analysis usually called a "crude oil assay". The assay of the raw material crude oils is a key factor in the selection of the unit processes required to achieve a desired refinery product slate. As stated previously, that means that the generation and composition of the refinery's wastewater depends upon the refinery's crude oil assay to a large extent.

To summarize, the key characteristics of a crude oil are:

- o Its boiling range components
- o Its sulfur and nitrogen content
- o Its PONA hydrocarbon analysis.

Those characteristics largely determine the unit processes required in refining the crude oil, and they vary quite considerably with the geographic location of the crude oil source.

Table 1 presents data on the sulfur content of crude oils relative to their geographic source on a worldwide basis. As shown in Table 1 (for the year 1974), 85 percent of the crude oils from Africa and 100 percent of the crude oils from Australasia are "low-sulfur" oils containing no more than 0.5 weight percent sulfur. In contrast, 47 percent of Middle Eastern and 71 percent of South American crude oils are "high-sulfur" oils containing more than 2.0 weight percent sulfur. On an overall weighted basis:

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TABLE 1. SULFUR CONTENT OF CRUDE OILS

	1974 Oil Production (bbls/day)	PERCENTAGE OF OIL PRODUCED			
		0.0-0.5 wt% S	0.51-1.0 wt% S	1.01-2.0 wt% S	> 2.0 wt% S
AFRICA	5,362,000	85.0	12.0	3.0	0.0
MIDDLE EAST	21,453,000	0.0	5.5	47.6	46.9
AUSTRALASIA [a]	1,773,000	100.0	0.0	0.0	0.0
EUROPE [b]	195,000	57.7	42.3	0.0	0.0
S. AMERICA	3,425,000	4.2	3.4	21.7	70.7
N. AMERICA [c]	10,956,000	57.8	7.5	26.3	8.4
TOTAL SOURCES	43,169,000	29.9	6.6	32.4	31.1

[a] Does not include China

[b] Does not include Russia

[c] Includes Canada, Mexico and U.S.A.

SOURCE: Thompson,C.J. et al, "Sulfur in World Crudes", Hydrocarbon Processing, February 1976

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29.9 percent of the world's crude oils contain no more than 0.5 weight percent sulfur.

6.6 percent of the world's crude oils contain between 0.5 and 1.0 weight percent sulfur.

32.4 percent of the world's crude oils contain between 1.0 and 2.0 weight percent sulfur.

31.1 percent of the world's crude oils contain more than 2.0 weight percent sulfur.

Table 2 (for the year 1978) presents similar data on the API gravity[a] of crude oils. About 50 percent of South American crude oils are heavier than 30° API and, in contrast, over 90 percent of Middle Eastern oils are lighter than 30° API. On an overall weighted basis:

1.9 percent of the world's crude oils are heavier than 20° API.

13.8 percent of the world's crude oils are between 20 and 30 °API.

71.4 percent of the world's crude oils are between 30 and 40 °API.

12.9 percent of the world's crude oils are lighter than 40° API.

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Tables 1 and 2 illustrate the very wide diversity and range of composition found among the world's major sources of crude oil.

A perspective on the amount of crude oil processed through U.S. refineries is provided in Table 3 and graphically presented in Figure 1. During the past six years:

- The number of U.S. refineries in operation has increased from 247 to 289.
- The national crude oil refining capacity has increased from about 14 million to about 17 million barrels per day.
- The total amount of crude oil actually processed has ranged between 12 million and 15 million barrels per day, representing 83 to 88 percent of the national refining capacity. In other words, there has been 12 to 17 percent of excess or unused refining capacity.
- The amount of imported crude processed in U.S. refineries has increased from 26 percent of the total oil processed to slightly over 40 percent.

The dependence of U.S. refineries on imported crude oil for a substantial part of their throughput will most probably continue for some time to come. Since a major part of those imports are from the Middle East, the sulfur content of the crude oils processed in

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[a] API gravity is inversely proportional to specific gravity. The higher the numerical value of API gravity, the lighter is the specific gravity.

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TABLE 2. API GRAVITY OF CRUDE OILS

	1978 Oil Production (bbls/day)	PERCENTAGE OF OIL PRODUCED			
		0-19.9 °API	20-30 °API	30.1-40 °API	> 40 °API
AFRICA	5,850,000	0.5	17.1	49.0	33.4
MIDDLE EAST	20,618,000	0.2	7.1	91.5	1.2
AUSTRALASIA [a]	2,698,000	0.5	11.5	57.9	30.1
EUROPE [b]	1,615,000	1.7	7.3	67.2	23.8
S. AMERICA	3,399,000	13.8	46.5	32.1	7.6
N. AMERICA [c]	11,043,000	2.4	16.2	61.6	19.8
TOTAL SOURCES	45,223,000	1.9	13.8	71.4	12.9

[a] Does not include China

[b] Does not include Russia

[c] Includes Canada, Mexico and U.S.A.

SOURCE: "Worldwide Production", Oil and Gas Journal, December 25, 1978

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TABLE 3. CRUDE OIL STATISTICS FOR THE REFINING INDUSTRY
(for the years of 1973-1978, inclusive)

During the year of:	Number of refineries	Crude oil refining capacity, b/d	Total amount of crude oil processed		Amount of domestic crude oil processed		Amount of imported crude oil processed	
			b/d	Percent of refining capacity	b/d	Percent of crude oil processed	b/d	Percent of crude oil processed
1973	247	14,216,000	12,452,000	87.6	9,208,000	73.9	3,244,000	26.1
1974	259	14,845,000	12,241,000	82.5	8,764,000	71.6	3,477,000	28.4
1975	256	15,075,000	12,480,000	82.8	8,375,000	67.1	4,105,000	32.9
1976	266	16,170,000	13,406,000	82.9	8,119,000	60.6	5,287,000	39.4
1977	285	16,849,000	14,727,000	87.4	8,179,000	55.5	6,548,000	44.5
1978	289	17,170,000	14,788,000	86.1	8,718,000	59.0	6,070,000	41.0

Note: All values of b/d are in average barrels per calendar day.

SOURCES: (a) "Forecast and Review", Oil and Gas Journal, January 29, 1979
(b) Annual Refining Issues of the Oil and Gas Journal for the years 1974 through 1979.

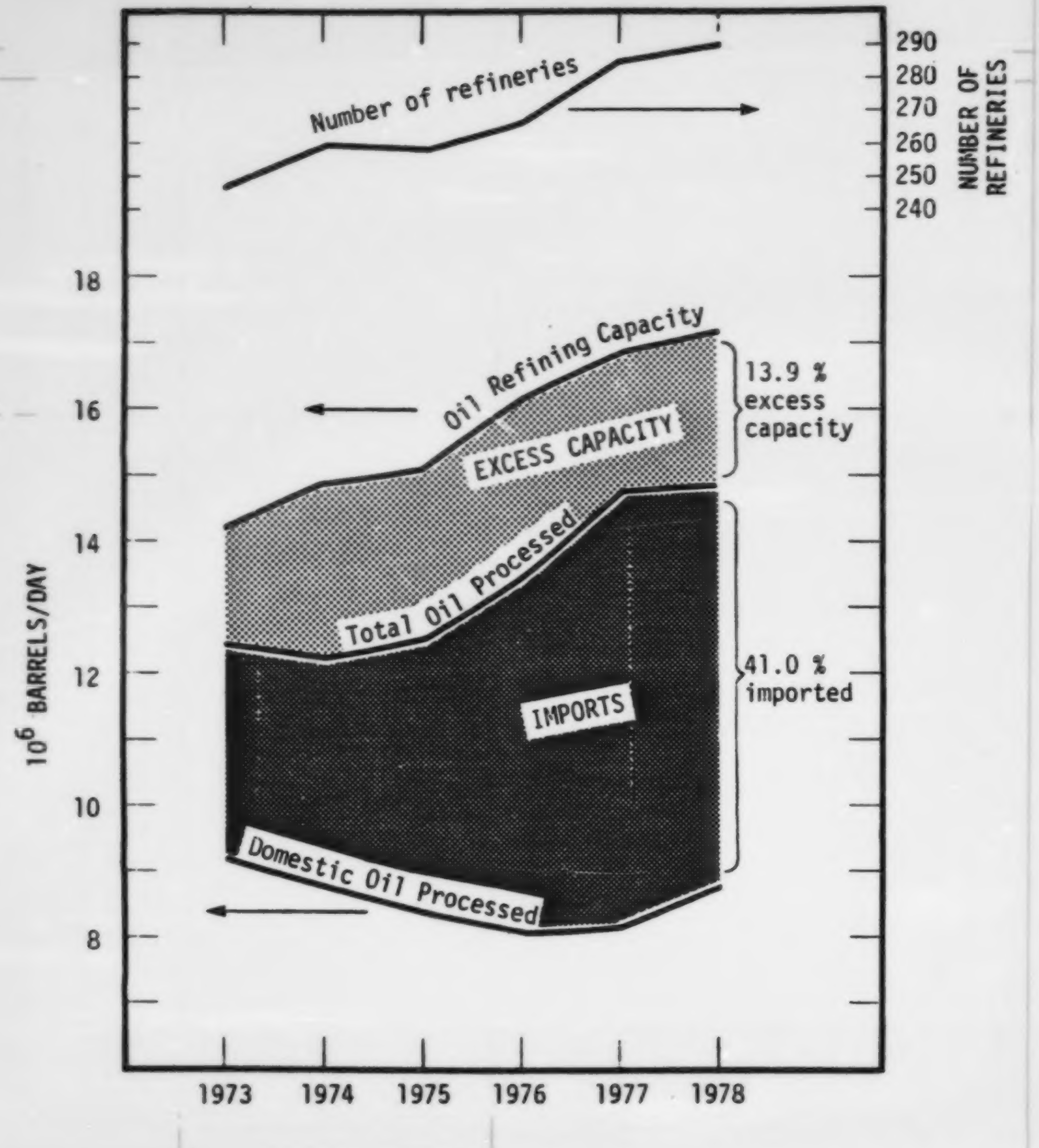

FIGURE 1. Crude oil statistics

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U.S. refineries will trend upward. As that occurs, U.S. refineries will have to install additional desulfurization facilities which will increase the generation of sour wastewaters. Additional hydrogen production facilities will also be needed to supply the need for hydrogen in the desulfurizers. Since hydrogen production units require large amounts of steam, there will be an increase in the fresh water demand of the refineries as well as an increase in wastewater steam blowdown and boiler feedwater demineralization wastes.

A study of the refining industry by the National Commission on Water Quality[2] in 1975 reported these average crude oil characteristics for refineries located in the districts defined in Figure 2:

District	Number of refineries*	Weight percent sulfur	API Gravity
1	29	1.16	34.3
2	70	0.68	36.3
3	104	0.52	35.3
4	30	0.97	35.3
5	56	1.07	32.6

(* As of January 1, 1979)

Although the above regional refining data on crude oil characteristics have probably changed somewhat since 1975, they serve to illustrate again the diversity of crude oils processed in U.S. refineries.

REFINING UNIT PROCESSES AND TECHNOLOGIES

A wide variety of unit processes and technologies are used in petroleum refineries. In general, they can be classified into four major groups:

- o Distillation is used to separate the crude oil into various boiling range fractions or "cuts". The crude oil is usually distilled in two steps, one at essentially atmospheric pressure and one at vacuum or reduced pressure conditions.
- o Cracking is used to convert long-chain hydrocarbon molecules (which are heavy, high-boiling oils) into shorter-chain hydrocarbons to increase the yield of lighter, lower-boiling products. There are three basic types of cracking:
  - (a) Thermal cracking which occurs under controlled conditions of high temperature and moderate pressure.
  - (b) Fluid catalytic cracking (FCC) which occurs in the presence of a fluidized catalyst and under controlled conditions of high temperature and pressure slightly above atmospheric.
  - (c) Hydrocracking which occurs in the presence of a fixed bed catalyst in a

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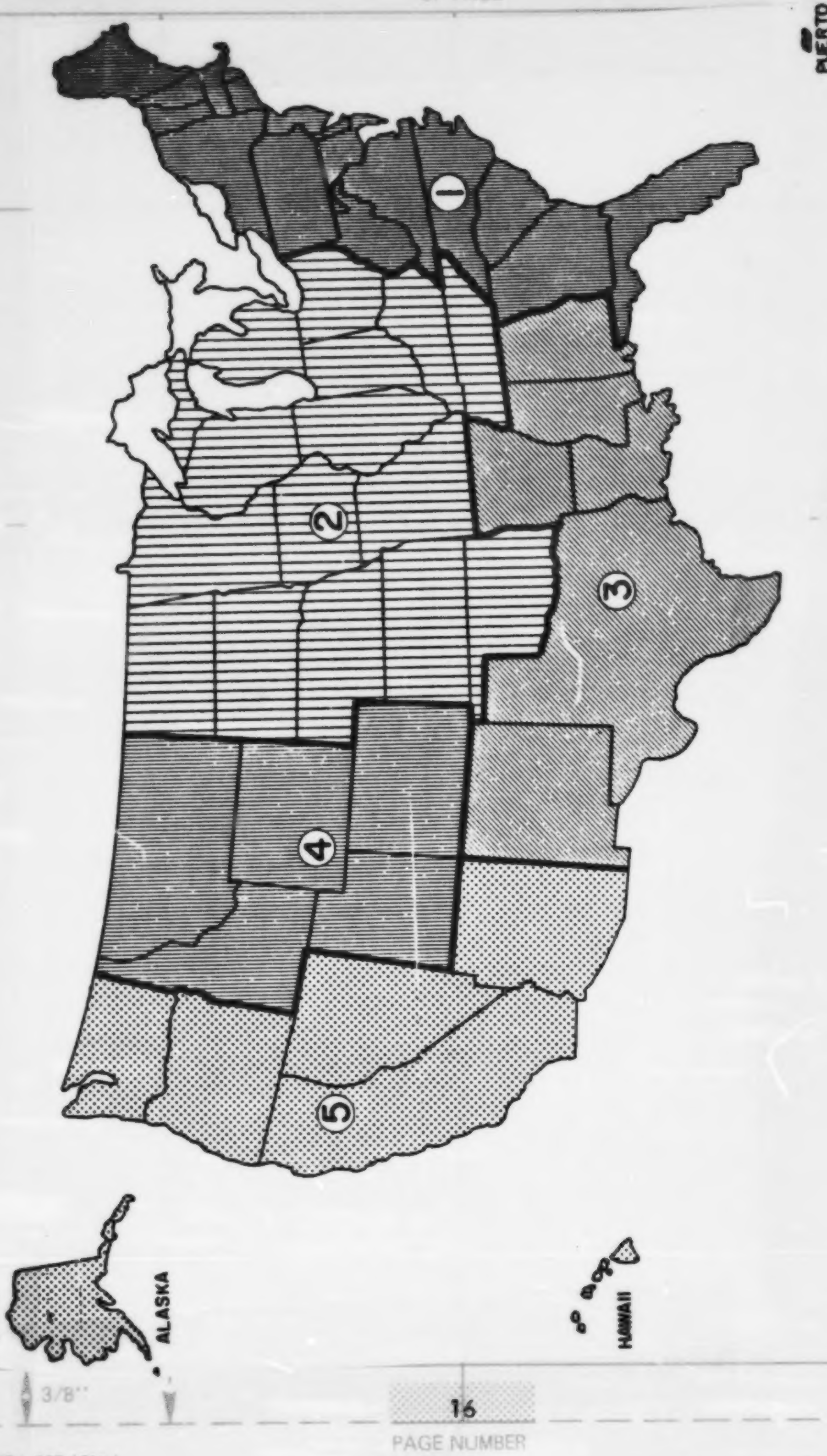
PUERTO RICO
1
2
3
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5
ALASKA
HAWAII

FIGURE 2. Petroleum Administration for Defense (PAD) districts

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hydrogen-rich vapor phase environment under controlled conditions of high temperature and high pressure.

- o Molecular Rearrangement Processes of many kinds are used to upgrade intermediate refining products by reshaping their molecular structures and to increase the yield of gasoline components by recombining hydrocarbons of three and four carbon atom chains into eight or nine carbon atom chains. The molecular rearrangement processes include catalytic reforming, catalytic alkylation, catalytic polymerization and catalytic isomerization...all of which will be discussed in more detail later in this section.

- o Desulfurization Processes are used to remove sulfur compounds from intermediate and endproducts. There are two basic types of desulfurization:

  (a) Catalytic hydrodesulfurization which converts organic sulfur compounds into hydrogen sulfide gas for subsequent removal by distillation or stripping. Catalytic hydrodesulfurization occurs in the presence of a fixed bed catalyst in a hydrogen-rich vapor phase environment under controlled conditions of temperature and pressure. This process also converts organic nitrogen compounds into gaseous ammonia which is subsequently removed along with the hydrogen sulfide, although the degree of nitrogen removal is usually not as high as that of sulfur removal. Catalytic hydrodesulfurization is sometimes referred to as "hydrotreating".

  (b) Non-catalytic scrubbing or washing of gases or hydrocarbon liquids with alkaline solutions for the removal of hydrogen sulfide and mercaptans, or for the conversion of mercaptans into less undesirable forms of sulfur. These so-called "treating" processes are used for scrubbing refinery gases as well as for liquids. The alkaline scrubbing of liquids also removes organic acids such as phenols, cresols and naphthenic acids which may be present.

The following discussions provide brief summaries of unit processes in each of the above groups and identifies their wastewater sources.

Atmospheric Crude Unit

The crude oil entering a refinery contains a small amount of emulsified brine ranging from 0.1 to 2.0 volume percent on the crude oil, and the brine may contain up to 25 weight percent salt (mostly sodium chloride)[1]. The salt content of the brine associated with the crude oil is usually expressed as pounds per thousand barrels of oil (p.t.b.) and the p.t.b. value ranges from 10 to 250 (as sodium chloride, NaCl). The sources of the emulsified brine are the naturally occurring brines associated with the original oil field and, in the case of oil transported by ocean-going tankers, contamination by sea water ballast in those tankers which are not provided with segregated ballast holds.

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Most refineries include crude oil desalters (which are either chemical or electrostatic de-emulsifiers) to remove the brine from the crude oil as it enters the atmospheric crude unit for processing. The crude oil is heated to about 250-300 °F and mixed with wash water (about 5 volume percent on the crude oil) to assist the desalting process. Typically, some caustic (NaOH) is also added to maintain a slightly alkaline pH level during the desalting.

The desalted crude is then further heated to about 700 °F and distilled into various boiling range fractions or "cuts". The distillation is done at essentially atmospheric pressure in what is commonly referred to as the "atmospheric crude unit" or, more simply, the "crude unit". The boiling range fractions produced in a crude unit are called "virgin" cuts since they are the naturally occurring components of the crude oil. The variety of virgin cuts that may be produced in a crude unit is specific to each refinery and its desired slate of endproducts. However, as a broad generality, the typical range of virgin cuts from a crude unit include:

- Propane and butane
- Light and heavy naphthas (raw gasoline components)
- Jet fuels and kerosines
- Diesel oils
- Light and heavy gas oils
- Heavy residual oil

Some of the raw virgin cuts must be stripped by injection of live steam in so-called "side-cut strippers" to reduce their ignition flash points. The stripping steam is subsequently condensed and removed from the overhead reflux drum of the crude unit's main distillation tower.

The two major sources of wastewater in a crude unit are the effluent brine from the crude oil desalter and the condensed stripping steam from the side-cut strippers.

Vacuum Unit

The heavy residual oil from the atmospheric crude unit is reheated to about 750 °F and is then further distilled under vacuum conditions so as to yield additional virgin boiling range cuts called vacuum gas oils.

Steam jet ejectors are usually used to achieve the required vacuum conditions. To prevent thermal degradation or coking of the heavy residual oil when it is heated to 750 °F, live steam is usually injected into the heater tubes as a diluent. Stripping steam is also injected into the bottom of the bacuum distillation tower to maximize the removal of volatiles. The steam used in the vacuum producing jet ejectors, the heater tubes and the bottom of the vacuum tower is subsequently condensed and removed from the overhead product drum of the tower. That condensed steam constitutes the major source of wastewater generated in a vacuum unit.

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The residual oil from the vacuum distillation unit is a heavy tar which typically has an atmospheric boiling point in excess of 800-1000 °F. In other words, all the virgin hydrocarbons in the crude oil with boiling points below 800-1000 °F are usually removed in the two distillation steps represented by the atmospheric crude unit and the vacuum unit.

Fluid Catalytic Cracking

Virgin gas oils produced from crude and vacuum distillation units have boiling ranges of about 600-1100 °F. Their molecules contain perhaps 18 or more carbon atoms and their molecular weights are in the range of 300 to 400. These gas oils can be processed and blended for endproduct use as industrial fuel oils. However, in many cases, it is more desirable to crack at least some of the virgin gas oils into lower-boiling molecules to increase the refinery yield of gasoline blending components.

Fluid catalytic cracking is one of the processes widely used to crack gas oils. The conversion[a] of virgin gas oils into lower-boiling materials by catalytic cracking is typically within the range of 75-90 percent. Some typical yields from virgin gas oil cracking are:

Gas	2-5 weight percent
Propane and propylene	8-12 volume percent
Butanes and butylenes	13-18 volume percent
Naphtha (gasoline)	60-65 volume percent
Gas oils	10-25 volume percent
Coke	4-8 weight percent

(the above yields are as percentages of the feed)

The catalytic cracking of gas oils occurs in a fluidized bed reactor under controlled conditions of temperature and flow at pressures slightly above atmospheric and in the presence of a fluidized catalyst. The coke yield deposits on the catalyst which is continuously circulated to a separate regenerator vessel where the coke is burned off of the catalyst. The heat of coke combustion is partially absorbed by the regenerated catalyst which returns to the fluidized bed reactor and provides a major portion of the required cracking reaction heat. The remainder of the heat requirement is supplied by a fuel-fired feedstock preheater.

The reaction yield mixture, which is in the vapor phase, then flows through a distillation tower where the yield mixture is cooled and distilled into its various boiling range cuts (see above typical yields). The hydrocarbon cracking reaction also cracks organic sulfur and nitrogen compounds contained in the virgin gas oil feedstock. Thus, the gas yield typically includes hydrogen sulfide as well as some ammonia, cyanides and thiocyanates.

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[a] Defined as the disappearance of gas oil boiling range material.

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Steam is used in the fluidized reactor to strip volatiles from the spent catalyst and some stripping steam may also be used in the reaction yield distillation tower. The steam is subsequently condensed and removed from the overhead drum of the distillation tower. Since that condensation occurs in intimate contact with the gas yield, the condensed steam contains some hydrogen sulfide, ammonia, cyanides and thiocyanates.

The cracking reaction also produces monohydric and dihydric phenols and thiophenols. Since some of those phenolics boil in the same temperature range as the yield naphtha, they are condensed along with the naphtha, gas and steam in the distillation tower overhead drum. And since the phenolics are water soluble, a portion of the phenols appears in the steam condensate from the overhead drum[1].

In summary, the steam condensate from the fluid catalytic cracking distillation tower overhead drum is the major wastewater source from a fluid catalytic cracking unit and it will usually contain:

- Hydrogen sulfide and ammonia in the form of ammonium hydrosulfide
- Cyanides and thiocyanates
- Phenols and thiophenols.

Hydrocracking

Hydrocracking process units are used for essentially the same purpose as fluid catalytic crackers, and that is to upgrade high-boiling gas oils by cracking them into lower-boiling materials. However, hydrocracking accomplishes both cracking and hydrogenation. Thus, the hydrocracking yield products are essentially saturated hydrocarbons with high concentrations of isoparaffins and naphthenes...whereas the fluid catalytic cracking products are essentially unsaturated with high concentrations of olefins.

The gas oil feedstock to a hydrocracker is heated to 500-900 °F and passed over fixed beds of catalyst at pressures ranging from 700 to 3000 psig in a hydrogen-rich vapor environment. By selection of the proper catalyst and the proper operating conditions, hydrocrackers may be designed so as to operate in either of these two optional product slate modes (or to have the flexibility of shifting from one mode to the other):

- A mode which maximizes the yield of naphthas (gasoline components within the boiling range of 100-400 °F).
- A mode which maximizes the production of middle distillates such as jet fuels, kerosene, diesel oil and light gas oil.

The vapor phase reaction products from the fixed-bed hydrocracking reactors are cooled and partially condensed by exchanging heat with the incoming feedstock followed by air or water-cooled exchangers. The reaction products are then reduced in pressure by stage-wise flashing. Part of the flashed, hydrogen-rich vapor is recompressed and recycled to the reactors. Makeup hydrogen is provided to replace the hydrogen

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consumed by the hydrogenation reactions. The remainder of the flashed vapor is subsequently processed to recover propane and butane. Water is injected continuously into the reaction product heat exchange and cooling train to wash out any buildup of salts or other foulants.

The liquid phase from the final flash stage is distilled in so-called stabilizers to remove residual propane and butane for subsequent recovery. The stabilized liquid product is then further distilled to provide the boiling range cuts consistent with the selected product slate mode of operation (see above).

Because of the hydrogenation which occurs in hydrocracking, a high percentage (as much as 85 percent or more) of the organic sulfur and nitrogen compounds in the hydrocracker feedstock gas oils is converted to gaseous hydrogen sulfide and ammonia. Under the high operating pressures existing in hydrocrackers, the partial pressure of the hydrogen sulfide and ammonia are such that they are largely absorbed into the wash water used in the reaction product heat exchanger train. Thus, the sour wash water withdrawn from the reaction product flash stages constitutes the major source of wastewater from a typical hydrocracker. The ammonium hydrosulfide content of that wastewater may be as high as 1-3 percent (10,000 to 30,000 ppm). That contrasts with the wastewaters from a fluid catalytic cracking unit which rarely contain more than 3000-5000 ppm of ammonium hydrosulfide. However, because of the hydrogenation reactions and because very little if any free oxygen is present in a hydrocracker, the hydrocracker wastewater should not contain any phenols...nor is there any evidence of cyanides or thiocyanates being present.

Thermal Cracking -- Delayed Coking

Thermal cracking processes are those in which cracking is induced simply by the proper selection of temperature and pressure conditions without using any catalyst or hydrogen. Three types of thermal cracking are in active use today: delayed coking, fluid bed coking and visbreaking.

Coking is a more severe form of cracking than visbreaking. The feedstock is usually a residual oil from a vacuum distillation unit and the purpose of coking is to convert that oil completely into cracked vapor and solid coke. In the delayed coking process, the residual oil feedstock is heated to about 900-950 °F under a pressure of about 20-60 psig and in the presence of some steam injected into the heater coils. Part of the thermal cracking occurs in the heater coils and the remainder occurs when the partially vaporized oil from the heater passes into very large vertical "coking drums". The complete conversion of the oil into cracked vapor and coke occurs through successive cracking and polymerization in the coking drums. The coke deposits itself on the walls of the coking drums. A delayed coker utilizes at least two drums, with one in onstream coking service while the other is being decoked by high-pressure water jets. The amount of coke produced from some delayed cokers in U.S. refineries is as much as 1500 to 3000 tons per day, although there are many smaller units as well.

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The cracked vapor flows from the coking drums to a distillation tower where it is cooled and distilled into various boiling range cuts (very similar to the distillation tower in a fluid catalytic cracker). As with the fluid catalytic cracker, the coker product gas and liquids are unsaturated with a high percentage of olefins.

The steam injected into the feedstock heater as well as stripping steam used in the distillation tower (and any associated side-cut strippers) is condensed and removed from the distillation tower overhead drum. That steam condensate is one of the major wastewater sources from a delayed coker and it contains the same contaminants as found in the wastewaters from a fluid catalytic unit: ammonium hydrosulfide, phenols and thiophenols, and cyanides and thiocyanates.

The periodic decoking of a coke drum involves a depressuring or "blowdown" step prior to opening the coke drum. The blowdown vapor is usually routed first into the coker distillation tower and then into a circulating quench tower for cooling the vapor. Depending upon the specific unit design, the circulating quench system may involve water which might result in another source of oily, sour and phenolic wastewater. However, it is very difficult to generalize the various designs employed for quenching coke drum blowdown vapors.

The high-pressure jet water used to drill the product coke from the coking drums is usually recovered for reuse as decoking water. If it is not completely recovered and reused, it constitutes a major, potential source of wastewater contaminated with coke particles, heavy oil, tar and probably phenols.

Thermal Cracking -- Fluid Bed Coking

Fluid bed coking serves the same function as delayed coking, which is to convert the heavy residual oil from vacuum distillation into cracked vapor and solid coke.

In a fluid bed coker, the residual oil feedstock is heated to about 950-1000 °F (much the same as for a delayed coker) and then enters a reactor which has a bed of hot, fluidized coke. In the reactor, the residual oil feedstock is completely cracked into vapor and product coke. The product coke becomes part of the fluidized coke bed which is continuously circulated to a coke burner vessel in which about 20-30 percent of the product coke is burned. The heat from the coke combustion is partially absorbed by the circulating, fluidized coke which returns to the reactor and provides most of the heat required by the cracking reactions. The net product coke is withdrawn continuously from the coke burner vessel.

The cracked vapor from the coking reactor flows through a quench section to a distillation tower where it is cooled and distilled into various boiling range cuts (very similar to the distillation tower in a fluid catalytic cracker). As with the fluid catalytic cracker or the delayed coker, the product gas and liquids from a fluid coker are unsaturated and have a high percentage of olefinic hydrocarbons.

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Steam is injected into the bottom of the reactor to strip volatiles from the circulating, fluidized coke. That steam as well as any stripping steam used in the distillation tower (and any associated side-cut strippers) is condensed and removed from the distillation tower overhead drum. The condensed steam is the major source of wastewater from a fluid bed coker and it contains the same contaminants as found in the wastewaters from fluid catalytic cracking or delayed coking: ammonium hydrosulfide, phenols and thiophenols, and cyanides and thiocyanates.

There is a variant of the fluid coking process, known as Flexicoking, which utilizes an integrated coke gasifier to produce refinery fuel gas from the net coke product withdrawn from the coke burner. Very few, if any, Flexicoking units have been installed in U.S. refineries as yet.

As a matter of interest, all of the delayed cokers in U.S. refineries are processing a total of about 940,000 barrels per day of residual oil and producing about 40,000 tons per day of coke. In contrast, fluid bed cokers in U.S. refineries are processing a total of about 70,000 barrels per day of residual oil and producing about 2500 tons per day of coke[3].

Thermal Cracking -- Visbreaking

Visbreaking is a relatively mild thermal cracking process. The purpose of visbreaking is to convert high viscosity residual oils (from either atmospheric or vacuum distillation units) into a lower viscosity fuel oil while minimizing the amount of naphtha formed.

The residual oil feedstock is heated to the range of 850-950 °F and mildly cracked in a fired heater. The heater effluent is quenched and distilled into the desired boiling range cuts. A typical range of cuts includes gas, naphtha, light fuel oil and heavy fuel oil.

Steam used in the cracking heater and the distillation tower side-cut strippers is condensed and removed from the distillation tower overhead drum. That steam condensate is a wastewater source containing sulfides and phenols.

In some cases, the heavy fuel oil from the bottom of the distillation tower is vacuum distilled to recover additional light fuel oil. In those cases, there may be another wastewater source originating with the required vacuum-producing steam jet ejectors.

There are less than a dozen visbreakers still operating in U.S. refineries and many of those are in relatively small refineries.

Steam Cracking (Olefins Production)

Steam cracking of hydrocarbons to produce ethylene and other olefins is a

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thermal cracking process which can be operated across a wide range of cracking severity on feedstocks ranging from gaseous ethane to heavy gas oils from vacuum distillation. Steam cracking produces ethylene, propylene, butadiene, aromatics and other by-products, all of which are used as precursor feedstocks in the manufacture of a broad spectrum of petrochemicals, plastics, synthetic rubbers and polymers. Since the primary product is considered to be ethylene, steam crackers are often referred to as "ethylene crackers".

Steam cracking of light hydrocarbon feedstocks such as ethane, propane and butane is less costly than steam cracking heavier feeds such as gas oils. The lighter feeds also provide a higher yield of the primary product ethylene. For example, steam cracking of ethane provides about an 85 percent ethylene yield whereas steam cracking of gas oils provides about a 22-26 percent yield of ethylene. For that reason, the largest part of the U.S. ethylene production is from light feedstocks. However, the availability of light hydrocarbon feeds for ethylene production is becoming increasingly difficult and gas oils can be expected to assume a larger percentage of the feedstock role in the future.

As a brief perspective of the U.S. ethylene production picture (as of 1976):

	Percent of total U.S. ethylene production	Number of steam crackers
Distribution by industry:		
13 chemical companies	53	33
10 petroleum companies	47	18
Distribution by feedstock type:		
Butane and lighter hydrocarbons	81.3	
Naphthas	7.8	
Gas oils	10.9	

As of January 1979, there were steam crackers in 14 U.S. refineries using gas oil feedstocks[3] totalling to about 150,000 barrels per day. Assuming that those units were achieving 22-26 percent yields of ethylene, their total annual ethylene production would be about four billion pounds per year which amounts to perhaps 12-13 percent of the current national annual ethylene production.

The feedstock to a steam cracker is heated and cracked, in the presence of a considerable amount of diluent steam, in tubular pyrolysis furnaces. The cracked products exit the furnaces at temperatures in the range of 1500-1700 °F and are rapidly quenched to prevent excessive cracking. The quenched vapors are further cooled in a distillation tower which removes the product fuel oil from the cracked vapors. The cooled vapors are then compressed to about 500-600 psig in multistage compressors with interstage cooling. Liquids comdensed interstage are removed and processed for recovery of liquid products. The compressed gases are treated for removal of acid gases (hydrogen sulfide and carbon dioxide), dried, refrigerated and fractionated for recovery of gas

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products.

A fairly typical product yield distribution when steam cracking gas oils is:

		weight percent on feed
Hydrogen-rich gas		1.5
Methane-rich fuel gas		10.5
	Total gas	12.0
Ethylene		26.2
Propylene		14.6
Butanes and butylenes		5.2
Butadiene		5.1
	Total C4's	10.3
Benzene-toluene-xylene		11.1
Non-aromatics		7.8
	Total gasoline	18.9
Fuel oil		18.0
	Total products	100.0

The design configuration, cracking severity and feedstock type vary quite considerably from unit to unit. It is therefore very difficult to be specific about the wastewater sources from steam cracking. However, as with any thermal cracking process in the presence of steam, there will be a sour, phenolic wastewater generated. In some designs, that wastewater may be reused (at least to some extent) as boiler feedwater for steam generation. There may also be these additional sources of wastewater generation: (a) spent caustic solution from the caustic washing of the cracked vapors at some interstage point in the compression train, and (b) an alkaline wastewater from the acid gas removal system.

Interim Summary

The unit processes discussed thus far are all within the first two major groups of refining processes and technologies, namely distillation and cracking processes. Functionally, those two groups involve:

- Distillation of a refinery's crude oil feedstock to separate the crude oil into its component fractions or boiling range cuts.
- Cracking the long-chain crude oil fractions (those which have boiling ranges higher than that of diesel oil) into shorter-chain gases and liquids.

However, the gases and liquids derived from distillation and cracking are only intermediate products which must undergo further processing to optimize the yield and quality

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of a refinery's endproduct slate. For example:

- Most of the intermediate products must be desulfurized either to meet end-product sulfur specifications or to make them suitable for further processing.
- Many of the intermediate naphthas can be improved by reshaping their molecular structure to increase their gasoline octane rating.
- The aromatics content (benzene, toluene, xylene) of many of the intermediate naphthas can also be increased by molecular reshaping, which increases the refinery's potential for producing petrochemicals.
- The short-chain propylene and butylene products from cracking can be converted to longer-chain, high octane gasoline components.

All of the processes summarized in the remainder of this section are either desulfurization or molecular rearrangement processes...in essence, processes which upgrade the intermediate products from distillation and cracking.

Catalytic Reforming

The spark-ignited, internal combustion engine used in most automobiles performs best with a gasoline fuel which burns smoothly rather than exploding. If the fuel explodes, the engine is heard to "knock" or "ping" and the engine performance deteriorates. The molecular structure of a gasoline determines its burning characteristics. Gasoline molecules of branched paraffins (isoparaffins) or saturated rings (aromatics) burn more smoothly than straight-chain paraffins (normal paraffins) or unsaturated rings (naphthenes). Thus, the anti-knock quality of gasoline is increased by increasing its isoparaffinicity and its aromaticity. The physical scale of anti-knock quality is measured by the "octane number" which is based on the iso-octane molecule having an octane number of 100. Thus, a gasoline with a 95 octane number rating has an anti-knock quality that is 95 percent as good as the anti-knock quality of iso-octane.

Hydrocarbon molecules in the gasoline boiling range of 100-400 °F have five to eight carbon atoms. As an example of the octane number of such molecules:

	Structure	Carbon atoms	Octane number*
Pentane	normal paraffin	5	62
Cyclopentane	naphthene	5	85
2-methylbutane	isoparaffin	5	90
Hexane	normal paraffin	6	26
Cyclohexane	naphthene	6	77
2,3-dimethylbutane	isoparaffin	6	94
Benzene	aromatic	6	115

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	Structure	Carbon atoms	Octane number*
Heptane	normal paraffin	7	0
3,3-dimethylpentane	isoparaffin	7	87
Toluene	aromatic	7	104
2,2,4-trimethylpentane**	isoparaffin	8	100
o-Xylene	aromatic	8	120

(* motor method; ** iso-octane, the octane number base)

As can be seen above, the octane numbers increase as the molecular structure for a given number of carbon atoms changes from paraffinic or naphthenic to isoparaffinic or aromatic.

The octane numbers of the virgin naphthas from a crude unit depend upon their PONA analyses and will vary from one crude source to another. However, in most cases, their octane numbers are not high enough to satisfy today's gasoline requirements. The octane numbers of catalytically cracked or thermally cracked naphthas are relatively good, but they can still be upgraded significantly. The same is true for the heavier portion of hydrocracked naphthas.

In most refineries, the primary purpose of the catalytic reforming process is to upgrade the octane numbers of virgin and cracked naphthas by increasing their isoparaffinicity and aromaticity. In some cases, catalytic reforming is used to increase the yield of aromatics for petrochemical usage as well as for gasoline octane improvement.

The naphtha feedstock to a catalytic reformer must first be desulfurized to very low levels, a few ppm or less, to avoid deactivation or "poisoning" of the reforming catalyst. The naphtha is then vaporized and heated to the range of 900-1000 °F under pressures of 150-500 psig and passed through fixed catalyst beds in a hydrogen-rich vapor environment. Although a number of reactions occur during reforming, the predominant ones are the dehydrogenation of naphthenes to form aromatics and the branching of paraffins to form isoparaffins. The dehydrogenation reactions make the reformer a net producer of hydrogen...in other words, a source of hydrogen for other refining processes which consume hydrogen.

The catalytic reaction products are cooled, partially condensed and separated into gas and liquid. A portion of the hydrogen-rich gas is recompressed and recycled to the reactors. The remainder enters the refinery's hydrogen supply system for use in other process units. The reaction product liquid is then fractionated to remove propane and butane for subsequent recovery. The final "reformate" gasoline is sent to storage as a blending component of the refinery's endproduct gasolines.

Since the naphtha feedstock to a catalytic reformer is desulfurized and water-free, and since no steam injection or water washing is used in a reformer, there is

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usually no source of wastewater in a reformer.

Catalytic Hydrodesulfurization -- Naphtha

Catalytic hydrodesulfurization is used to remove sulfur from virgin and cracked naphthas[a] which are to be catalytically reformed. The catalytic hydrodesulfurization process converts organic sulfur into gaseous hydrogen sulfide which is then removed by stripping or distillation.

The naphtha feedstock to a catalytic hydrodesulfurization unit is vaporized and heated to the range of 400-700 °F under pressures of 200-500 °F and passed through fixed catalyst beds in a hydrogen-rich vapor environment. Hydrogenation is the predominant reaction that occurs. Thus, organic sulfur and nitrogen in the naphtha feedstock are converted to gaseous hydrogen sulfide and ammonia. Olefinic hydrocarbons in the naphtha feedstock[b] are also hydrogenated or saturated to some extent. The hydrogen consumed by the hydrogenation reactions is usually supplied by the excess hydrogen produced in the subsequent catalytic reforming of the naphtha.

The reaction products are cooled, partially condensed and separated into gas and liquid. The hydrogen-rich gas is recompressed and recycled to the reactors, along with makeup hydrogen (usually from a reformer) to replace the hydrogen consumed in the hydrodesulfurization reactions. The reaction product liquid is then stripped to remove hydrogen sulfide, ammonia and other gases. After distillation to remove propane and butane for subsequent recovery, the hydrodesulfurized naphtha is sent to a catalytic reformer.

As noted earlier herein, the primary purpose of a naphtha hydrodesulfurization unit is to remove sulfur down to levels of no more than a few ppm so as to prevent catalyst poisoning in the subsequent catalytic reforming of the naphtha. The same is true of water in that the naphtha feed to reforming must be essentially completely free of water. Any water in the desulfurized naphtha after stripping would be withdrawn from the overhead drum of the distillation tower which removes propane and butane. That overhead water is a source of sour wastewater from most naphtha hydrodesulfurization units. If wash water is injected into the reaction product heat exchange train (similar to the operation described earlier herein for catalytic hydrocrackers), then that water will absorb hydrogen sulfide and ammonia and constitutes another source of sour wastewater from the hydrodesulfurization process. If the hydrodesulfurization feedstock includes catalytic or thermally cracked naphthas, there is some possibility (although slight) that the hydrodesulfurization sour wastewater may contain some phenols.

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[a] With the exception of hydrocracked naphthas which are thoroughly desulfurized during their formation in the hydrocracker.

[b] Virgin naphthas would not contain olefins since crude oils rarely include olefinic hydrocarbons. Nor would hydrocracked naphtha have any olefins since they would have been hydrogenated in the hydrocracker. Catalytic and thermally cracked naphthas would have high olefin contents.

Catalytic Hydrodesulfurization -- Distillates

Catalytic hydrodesulfurization is often used to remove sulfur and nitrogen from a variety of virgin and cracked distillate oils in the boiling range of jet fuels, kerosines, diesel oils and light fuel oils in order to satisfy the pertinent market specifications for those products. If the distillate oil feedstock contains cracked, olefinic material, then catalytic hydrodesulfurization can also be used to hydrogenate or saturate a portion of the olefins to improve the color, odor and oxidation stability of the product.

The catalytic hydrodesulfurization process for distillate oils is very similar to that for naphthas except that, in general, the distillate oil process requires a higher reaction temperature and pressure and consumes more hydrogen.

The sour wastewater sources from a distillate hydrodesulfurization are essentially the same as from a naphtha hydrodesulfurization unit.

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Catalytic Hydrodesulfurization -- Heavy Oils

Catalytic hydrodesulfurization units may also be used in refineries to desulfurize and denitrify heavy oils such as:

- Gas oil feedstocks to fluid catalytic crackers, which is considered to improve the performance of the catalytic cracking unit.
- Gas oil feedstocks to hydrocrackers, to provide a prior removal of sulfur and nitrogen.
- Heavy gas oils and residual oils (from both atmospheric and vacuum distillation units) to produce low-sulfur industrial fuel oils.

The catalytic hydrodesulfurization process for heavy oils is similar to that for naphthas and for distillate oils except that the heavy oil process, in general, requires a higher reaction temperature and pressure and it consumes more hydrogen. In fact, the catalytic hydrodesulfurization process for very heavy oils requires temperatures and pressures as high or higher than those required in catalytic hydrocracking (500-900 °F and 700-3000 psig).

The sour wastewater sources from a heavy oil hydrodesulfurization unit are the same as from a naphtha or distillate oil hydrodesulfurization unit.

All of the various catalytic hydrodesulfurization processes for naphthas, distillates and heavy oils are ofen referred to as "hydrotreaters".

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Gas Recovery Plants

Almost all of the refinery unit processes yield a byproduct gas. In general, olefin-rich gases are produced by thermal and catalytic cracking while saturated (paraffinic) gases are produced by hydrocracking, catalytic reforming and hydrotreating. The typical byproduct gas components and their sources are:

Hydrogen --

Catalytic reformers and hydrogen synthesis units are the major sources of hydrogen in most refineries. Other sources of hydrogen production are thermal and catalytic cracking.[a]

Hydrogen sulfide --

Hydrogen sulfide, derived from the cracking and hydrogenation of organic sulfur contained in crude oil, appears in the byproduct gases from thermal cracking, catalytic cracking and hydrotreating. A small amount of free hydrogen sulfide may also be distilled from the crude oil in an atmospheric crude unit.

Ammonia --

Ammonia is derived from the cracking and hydrogenation of organic nitrogen contained in crude oil. Because of its very high solubility in water, a large part of the ammonia appears in the wastewaters from the various process units rather than their byproduct gases. If both ammonia and hydrogen sulfide are present, the ammonia appears in the wastewater as ammonium hydrosulfide.

Carbon dioxide --

A small amount of carbon dioxide appears in the byproduct gas from fluid catalytic cracking, derived by entrainment of carbon dioxide in the fluidized catalyst circulated from the fluid catalytic cracking coke-burning regenerator to the fluid catalytic cracking reactor. Carbon dioxide also appears in the byproduct gas from fluid coking for much the same reason.

Methane and ethane --

The byproduct gases from atmospheric and vacuum distillation of crude oil contain small amounts of methane and ethane, some of which is virgin gas distilled from the crude oil and some of which results because of a slight amount of thermal cracking which occurs in the distillation heaters. All of the cracking processes (thermal, catalytic and hydrocracking) as well as catalytic reforming yield methane and ethane in varying amounts.

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[a] Hydrogen also appears in the byproduct gases from hydrocracking and hydrotreating. However, those processes are not hydrogen producers. The hydrogen appears only because it is brought in to maintain the required hydrogen-rich environment for those processes.

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Ethylene --

Ethylene is an olefin and is yielded by all of the various thermal cracking processes (delayed and fluid coking, visbreaking, steam cracking) and by fluid catalytic cracking.

Propane, normal butane and isobutane --

Any virgin propane and butanes in the crude oil appear in the byproduct gas from an atmospheric crude unit. Thermal cracking, catalytic cracking and hydrocracking all yield propane and butanes in varying amounts, as does catalytic reforming. In general, the propane yield from the various processes appears almost completely in their byproduct gases. However, some of the butane yield may be retained in the naphtha products from the processes. In other words, the stabilization (distillation) of the liquid naphthas to remove propane and butane usually removes all of the propane but leaves a small amount of butanes in the naphthas.

Propylene, normal butylene, isobutylenes and butadiene --

These are all olefins and they are yielded by all of the cracking processes, either thermal or catalytic. None of the hydrogen-environment processes (catalytic reforming, hydrotreating, hydrocracking) produce any olefinic gases. [Thus, although thermal and catalytic cracking produces both olefinic and saturated gases, the hydrogen-environment processes produce only saturated gases.] In general, the propylene yield from the various processes appears almost completely in their byproduct gases. However, some of the butylene and butadiene yield may be retained in the naphtha products from the processes depending upon the degree to which the liquid naphthas are stabilized.

Normal pentane, isopentanes and pentylenes --

These are light hydrocarbons with five carbon atom chains and boiling within the range of 70-80 °F at atmospheric pressure. Under pressures slightly above atmospheric and temperatures of about 100 °F, these hydrocarbons are largely recovered as part of the various refinery naphthas. Small amounts of virgin normal and isopentane may appear in the byproduct gas from crude oil distillation units depending upon the operating conditions in the distillation tower overhead drum. Some normal and isopentane may also appear in the byproduct gas from most of the refining processes discussed herein depending upon their operating conditions for gas-liquid separation and upon their naphtha distillation conditions and sequence. The same is true of the olefinic pentylenes except that they will appear only in the byproduct gases from cracking processes, either thermal or fluid catalytic. Pentylenes are not produced by any of the hydrogen-environment processes.

The purpose of refinery gas recovery plants is to collect the byproduct gases from all of the unit processes and to separate them into various products. For example:

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Components of combined byproduct gases from refinery unit processes		
Name	Symbol	Separated products from gas recovery plant
Hydrogen	H_2	Acid gases (H_2S, CO_2)
Hydrogen sulfide	H_2S	Refinery fuel gas (H_2, C1, C2)
Ammonia	NH_3	C3 LPG (C3, $C3^{=}$)*
Carbon dioxide	CO_2	C4, LPG (iC4, C4, $iC4^{=}$, $C4^{=}$, $C4^{==}$)*
Methane	C1	Light naphtha (iC5, C5, $C5^{=}$)
Ethane	C2	
Ethylene	$C2^{=}$	
Propane	C3	
Propylene	$C3^{=}$	
Butane	C4	
Isobutane	iC4	
Butylenes	$C4^{=}$	
Isobutylenes	$iC4^{=}$	
Butadiene	$C4^{==}$	
Pentane	C5	
Isopentane	iC5	
Pentylenes	$C5^{=}$	

(* LPG is an acronym for "liquefied petroleum gas". The LPG cuts from a gas recovery plant may be marketed as an endproduct or further processed to produce naphtha.)

In a typical gas recovery plant, the byproduct gases from the various unit processes are compressed and then processed through an absorption system followed by a sequence of distillation towers.

The sour gas from the absorption system (the refinery fuel gas containing hydrogen sulfide and carbon dioxide) is then treated or scrubbed with an amine solution which absorbs and removes the acid gases (hydrogen sulfide and carbon dioxide) from the refinery fuel gas. The acid gases are subsequently distilled and removed from the amine solution, and the regenerated solution is recirculated for reuse in scrubbing additional sour gas. The C3 and C4 LPG cuts from the distillation towers are also scrubbed with amine for hydrogen sulfide removal. The amine treating of hydrocarbon gases and liquids for removal of hydrogen sulfide is often referred to as "sweetening". The acid gases from the amine regeneration (distillation) are subsequently processed for conversion into byproduct sulfur.

The sweetened refinery fuel gas is used as fuel in the refinery process heaters and steam-generating boilers. The LPG cuts may be marketed as endproduct fuels or further processed for conversion into high-octane gasoline components (as discussed later herein).

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After being further treated by alkaline scrubbing for removal of organic sulfur compounds known as mercaptans (as discussed later herein), the light naphtha is used as a blending component of the refinery's endproduct gasolines.

Many refineries include two gas plants, one of which handles predominantly saturated or paraffinic gases and one of which handles the predominantly olefinic gases. This permits the refinery to segregate its LPG cuts and light naphthas into those which are saturated and those which are olefinic or unsaturated.

In general, the wastewater sources from gas recovery plants fall into three categories:

- Water condensed from the incoming gases by compression interstage and after-stage cooling. The water from saturate gas plants will contain hydrogen sulfide and ammonia in the form of ammonium hydrosulfide. The water from unsaturate gas plants will contain cyanides, thiocyanates and perhaps some phenols in addition to ammonium hydrosulfide.
- Water removed from the overhead drum of the depropanizing tower in the distillation sequence. The water will contain hydrogen sulfide and perhaps traces of mercaptans.
- Water discharged from the amine scrubbing and regeneration system which will contain hydrogen sulfide and some of the amine. Typically, the amine in refinery usage is DEA (diethanol amine). The amount of wastewater from this source varies widely with the design of the amine treater, but it is generally fairly small.

Merox Treating

Mercaptans are a form of organic sulfur (denoted as RSH) found in many refinery streams. Merox treating is one of the many processes used for either removing mercaptans from liquid hydrocarbons or for converting them to disulfides (denoted as RSSR). Many of the treating processes use a caustic solution. Merox is a widely practised treating process which uses caustic, methyl alcohol and air in the presence of a catalyst. The Merox process may be designed for mercaptan extraction (removal) or for sweetening which is the conversion of the mercaptans to disulfides.

The wastewater sources from a Merox unit are the spent caustic discharged as well as spent wash water (when a final water wash is included in the design). Those wastewaters will contain sodium mercaptides (NaSH) derived from any hydrogen sulfide which might be present in the Merox feedstocks. The wastewaters from Merox treating of olefinic naphthas (from thermal crackers or fluid catalytic cracking units) will also contain sodium phenolates.

Alkylation Process

The alkylation process combines isobutane with propylene and/or butylenes to produce a very high-octane gasoline component known as "alkylate". The alkylation reaction occurs in the liquid phase and in the presence of either a sulfuric acid (H_2SO_4) or hydrofluoric acid (HF) catalyst.

One of the reasons for segregating the production of C3 and C4 cuts by using separate saturate and unsaturate gas plants is to facilitate the subsequent alkylation of the unsaturated propylene and butylenes with saturated isobutane.

The feedstock C3 and C4 cuts to an alkylation unit must first be treated for removal of hydrogen sulfide and mercaptans (by amine treating followed by caustic or Merox treating). In addition, the unsaturated C3 and C4 is usually processed through a catalytic hydrogenation unit to convert diolefinic butadiene into mono-olefinic butylene so as to avoid excessive consumption of the acid catalyst in the alkylation reaction. The pretreated liquid feedstocks are cooled and thoroughly mixed with liquid acid (a sulfuric acid alkylation reaction requires a refrigerated reaction zone). The reaction effluent is separated from the acid and distilled to provide these products:

- o Unreacted isobutane which is recycled to the reaction zone.
- o Unreacted propane and normal butane which constitute an LPG endproduct.
- o High-octane alkylate gasoline.

The reaction products from both sulfuric acid and hydrofluoric acid alkylation require the removal of entrained, residual acid. The exact mode of removal varies between the two processes, but they both generate wastewaters which contain traces of acid or acid salts (if caustic is used to neutralize the acid).

The spent acid from alkylation is carefully segregated and made available for regeneration in separate facilities. Normally, the spent acid does not enter the refinery wastewater system.

A hydrofluoric acid alkylation unit must be very carefully designed to prevent any escape of the extremely hazardous hydrofluoric acid. This is not to say that a sulfuric acid alkylation unit does not require careful design as well, but hydrofluoric acid is relatively much more hazardous than sulfuric acid.

Catalytic Polymerization

The catalytic polymerization process converts propylenes or propylenes and butylenes into C6 or C7 dimers (isohexenes and isoheptenes) which are within the gasoline boiling range and have good octane ratings. Some trimerization to C9 isononenes also occurs. The process is sometimes referred to as "dimerization", and the endproduct gasoline is referred to as "cat poly gasoline" or "dimer gaoline". The catalyst usually

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used in the process is phosphoric acid.

The sources of wastewater from a catalytic polymerization unit are spent caustic and spent wash water which are used to remove entrained acid from the reaction effluent. The wastewaters will contain some acid or acid salts.

Isomerization -- Butane

Butane isomerization is a process which converts normal butane to isobutane. It is used to supply additional isobutane for those refineries which lack sufficient isobutane to maximize the alkylation of their available propylene and butylenes.

Butane isomerization occurs over fixed catalyst beds at temperatures of 200-400 °F under pressures of 200-500 psig and in a hydrogen-rich vapor environment. The reaction effluent is cooled, partially condensed and separated into gas and liquid. The hydrogen-rich gas is recompressed and recycled to the reaction zone along with makeup hydrogen. The liquid is distilled to remove dissolved hydrogen as byproduct gas and to recover unreacted normal butane for recycle to the reaction zone. The product isobutane is sent to storage or directly to an alkylation unit.

isomerization -- Pentane and Hexane

Catalytic isomerization is also used to upgrade the octane rating of light, paraffinic naphthas which are rich in normal pentane and normal hexane by converting them into isopentane and isohexane. The process is almost identical to that described above for the isomerization of butane. The endproduct isopentane and isohexane is often referred to as "isom gasoline" or "isomerate".

Neither the butane nor the pentane and hexane isomerization processes produce any wastewaters under normal operation.

Hydrogen Synthesis

As noted earlier herein, the two major sources of hydrogen in most refineries are: (1) the catalytic reformers used for upgrading the octane numbers of naphthas and (2) hydrogen synthesis units. Of the two sources, catalytic reforming is by far the largest:

> As of January 1979[3], there were 36 refineries with hydrogen synthesis units producing an aggregate total of about 1.7 billion SCFD (standard cubic feet per day) of hydrogen. At the same time, there were 204 refineries with catalytic reformers processing an aggregate total of 3.8 million barrels per day of naphthas. Assuming an average hydrogen yield of 900 SCF per barrel of naphtha processed, the aggregate total hydrogen produced by catalytic reforming was 3.4 billion SCFD ...or twice that produced by hydrogen synthesis units.

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The various hydrogen synthesis processes in refinery usage include steam reforming of methane, steam reforming of naphtha and partial oxidation of residual oils. As of January 1979[3], steam reforming of methane accounted for the largest percentage of hydrogen synthesis:

Steam reforming of methane	81.2 percent
Steam reforming of naphtha	7.0 percent
Partial oxidation	6.0 percent
Others	5.8 percent

The steam reforming of methane-rich refinery gas or natural gas to produce hydrogen involves four steps:

- Reforming of methane and steam into hydrogen and oxides of carbon at temperatures of 900-1600 °F under pressures of 300-600 psig within the catalyst-filled tubes of a fired heater. The main reaction which occurs is:

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$

- Catalytic conversion or "shifting" of the carbon monoxide (yielded from the reforming reaction) into carbon dioxide as in this reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

- Cooling the shift reaction effluent gas and removing the carbon dioxide by scrubbing with monoethanol amine (MEA) or an equivalent acid gas absorbent.

- Catalytic conversion or "methanation" of any residual oxides of carbon into methane:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Theoretically, the combination of the reforming step and the "shift" conversion step requires two moles of steam for each four moles of hydrogen produced:

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$$

That amounts to a theoretical consumption of about 24,000 pounds of steam per million SCF of hydrogen produced. In actual practice, the steam fed to the reforming reaction is about twice the theoretical consumption. When the shift reaction effluent gas is cooled just ahead of the monoethanol amine scrubbing, the excess steam is condensed and removed. In a steam-methane reforming unit producing 50 million SCFD of hydrogen, the condensate removed is about 100 gpm. The condensate will be saturated with carbon dioxide and, if the feedstock contains nitrogen, some ammonia and cyanide may appear in the condensate. Many hydrogen synthesis plants are designed to reuse the condensate

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as boiler feedwater for steam generation in the plants' waste heat recovery systems. If not reused, the condensate constitutes the major wastewater source in a hydrogen synthesis plant.

Aromatics Extraction

As discussed previously, the naphtha produced by catalytic reforming has a high content of aromatics. In some refineries, the catalytic reformers are operated at conditions designed specifically to increase the yield of benzene, toluene and xylenes (which are the aromatics commonly referred to as BTX) for extraction as endproduct petrochemicals. In fact, as of January 1979[1], 38 refineries in the U.S. included extraction units producing an aggregate total of about 196,000 barrels per day of BTX.

There are many solvent extraction and extractive distillation processes for the removal and recovery of BTX from catalytic reformate. Typical BTX recoveries achieved in such processes are 99.9 percent for benzene, 99.5 percent for toluene and 98 percent for xylenes. Some of the solvents used for BTX extraction are:

- Tetramethylene sulfone (referred to as sulfolane)
- Tetraethylene glycol
- Morpholine derivatives such as formyl-morpholine.

The non-aromatics or "raffinate" from BTX extraction units is used either as an endproduct gasoline component or as feedstock for steam crackers (olefins production plants). In some cases, the raffinate may be marketed as a feedstock for gasification plants producing synthetic natural gas (SNG).

Xylene has three isomeric forms known as ortho-, meta- and para-xylene. Most of the endproduct market is for ortho- and para-xylene. There is little market, if any, for meta-xylene. Thus, many BTX extraction units are coupled with xylene isomerization units which are catalytic processes designed to isomerize meta-xylene and increase the yield of ortho- and para-xylene.

Many of the BTX extraction processes include washing of the BTX extract and the raffinate streams with water to recover entrained solvent. The solvent-rich water is then reprocessed to recover both the solvent and the water for reuse. Thus, in normal operation, BTX extraction does not generate a wastewater. Any liquid losses from an extraction unit (sample drains, pump and valve drips, maloperation, etc.) would contaminate the refinery wastewater sewers with the extraction solvent and/or the BTX aromatics.

Petrochemicals

Many refineries produce a range of petrochemicals among their endproducts. As discussed earlier, some refineries include the steam cracking of gas oils which produces

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petrochemicals such as ethylene, propylene, butadiene and BTX aromatics. And some refineries extract BTX aromatics from catalytic reformate. Many other petrochemicals are also produced in some refineries, with the more common ones being:

- Ethylbenzene -- produced by the catalytic reaction of benzene and ethylene.
- Styrene monomer -- produced by the catalytic dehydrogenation of ethylbenzene.
- Cumene -- produced by the catalytic reaction of propylene and benzene.
- Cyclohexane -- produced by the catalytic hydrogenation of benzene.

In addition to those above, a very broad spectrum of other petrochemicals are manufactured from feedstocks derived by the refining of petroleum crude oil. Almost every major oil company now has a petrochemical manufacturing division. Many oil companies have also expanded into the large-scale manufacture of ammonia and other agricultural chemicals. In many cases, the oil company's petrochemical plants are adjacent to their major refineries and it is very difficult to define the exact line of demarcation between their petroleum refining operations and their petrochemical manufacturing.

There are far too many permutations of products and processes to generalize as to the sources or composition of wastewaters from petrochemicals production. Each individual refinery's petrochemical operations must be evaluated on a specific case-by-case basis.

[The reader who wishes to gain a perspective on the range and extent of the petrochemical industry should read the excellent series of articles by Hatch and Matar[4].]

Lubricating Oils

About 40 U.S. refineries are currently producing lubricating oils with an aggregate output of approximately 230,000 barrels per day. The specifications for lubricating oils vary considerably and include endproducts for:

- Automotive uses:
  - (a) Engine oils and transmission fluids
  - (b) Brake and shock absorber fluids
- Marine and heavy-duty industrial engines
- Special uses:
  - (a) Transformer oils
  - (b) Refrigeration system oils
  - (c) Heat transfer oils
  - (d) Metal-working oils
  - (e) Agricultural spray oils

The key properties of a lubricating oil which must be "tailored" to produce the

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specifications needed for each of the above endproduct uses are:

- o The fluidity of the oil as defined by its viscosity.
- o The effect of temperature on the oil's viscosity as defined by its viscosity index (VI) (the less the viscosity changes with temperature, the higher or better is the viscosity index).
- o The low-temperature usefulness of the oil as measured by its pour point temperature which is a function of its wax content (the higher the wax content, the higher the pour point temperature at which the oil congeals and will not pour).

In general, the basestocks from which a refinery produces the lubricating oils are:

- o Vacuum gas oils (with boiling ranges of 650-1000 °F) produced from the refinery's vacuum distillation unit.
- o Vacuum residual oils (boiling above 1000 °F) from which the asphaltenes must first be removed by using propane or other hydrocarbon solvents. The removal of asphaltenes by propane or other solvents is called "solvent de-asphalting" and the de-asphalted oil is referred to as "SDA oil".

The viscosity index of the vacuum gas oil and SDA oil basestocks may be improved by solvent extraction of the aromatics and resins in the basestocks using any of these solvents:

- o Furfural
- o Phenol
- o Liquid sulfur dioxide (SO_2)
- o N-methyl-2-pyrrolidone (NMP)

Alternatively, catalytic hydrogenation may be used to saturate the aromatics and resins instead of solvent extraction.

The lubricating oils may be further processed for lowering of their pour points (to improve their low-temperature usefulness) by solvent extraction of waxes using any of these solvents:

- o Propane
- o Methyl ethyl ketone (MEK)
- o Urea
- o Propylene and acetone mixtures
- o Dichloroethane and methylene chloride mixtures
- o MEK and methyl isobutyl ketone (MIBK) or toluene mixtures

Catalytic hydrogenation may also be used as an alternative to the solvent extraction of waxes.

Basestocks derived from naphthenic crude oils usually require very little processing to produce lubricating oils with little wax and low pour points but relatively poor viscosity indexes. A typical naphthenic lubricating oil has these properties:

Viscosity at 100 °F	500 SUS (Saybolt Universal Seconds)
Viscosity at 210 °F	54-56 SUS
Viscosity Index	25-50
Pour Point	-15 °F

Catalytic hydrogenation may be used to improve the viscosity index of a naphthenic lubricating oil.

Paraffinic basestocks produce lubricating oils with good viscosity indexes but high wax contents and high pour points. After solvent extraction of aromatics and resins followed by solvent de-waxing, typical paraffinic lubricating oils have these properties:

	100 vis oil	300 vis oil
Viscosity at 100 °F	100 SUS	300 SUS
Viscosity at 210 °F	39.5 SUS	52 SUS
Viscosity Index	95	95
Pour Point	0 °F	0 °F

The lubricating oils produced from SDA vacuum residual oil are called "bright stocks" or "cylinder stocks". After solvent extraction of aromatics and resins followed by solvent de-waxing, a typical bring stock has these properties:

Viscosity at 100 °F	2650 SUS
Viscosity at 210 °F	155 SUS
Viscosity Index	95

The variety of process options and sequences practiced in lubricating oil production makes it very difficult to generalize as to the source and composition of their wastewaters. However, there is an obvious potential for any of these solvents to enter the refinery's wastewater sewers: furfural, MEK, MIBK, toluene, phenol, urea, NMP, acetone and others.

Asphalt Production

The petroleum refining industry produces a variety of asphalts or bitumens. The primary end use for asphalt is in the paving of roads. Some specialty uses (roofing tar, flooring tiles, etc.) account for a relatively small amount of the asphalt market. About 95 U.S. refineries currently produce an aggregate total of about 800,000 barrels per day of asphalt.

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Asphalt is produced by the oxidation of asphaltic, vacuum residual oils. The oxidation is accomplished by blowing air through the heated residual oil. The hot gases from the air blowing are cooled by direct quenching with steam and water, which produces a very oily wastewater. If any cracking occurs during the air blowing, the wastewater will probably contain some heavy phenolic materials.

Sulfur Recovery

Many refineries convert their hydrogen sulfide-rich gases into byproduct sulfur by using a catalytic process commonly known as the Claus process. As discussed earlier herein, hydrogen sulfide is removed from refinery gases and from C3 and C4 cuts by absorption in an amine solution. The subsequent regeneration of the spent amine for reuse (by distilling the spent amine) yields a concentrated hydrogen sulfide gas. That hydrogen sulfide-rich gas from amine regeneration typically constitutes the major part of the hydrogen sulfide fed to a Claus process.

The Claus process usually consists of a combustion step followed by two or three fixed-bed catalyst stages. About one-third of the incoming hydrogen sulfide is burned to form sulfur dioxide in the combustion step:

$$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O$$

The sulfur dioxide then reacts with the remainder of the hydrogen sulfide in the fixed-bed catalyst stages to yield byproduct sulfur:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

The reaction effluent is cooled to the melting point of sulfur and the condensed, molten sulfur is withdrawn and sent to storage. The residual gases are either incinerated or further processed (in so-called "tail gas" units) for additional sulfur recovery.

Normally, the Claus process does not generate any wastewater. The water vapor in the reaction effluent (see above reactions) remains in the tail gases which are vented to the atmosphere after incineration or further tail gas processing.

Sour Water Strippers

The term "sour wastewater" refers to any wastewater which contains either:

- Dissolved hydrogen sulfide, or
- Hydrogen sulfide and ammonia combined in the form of ammonium hydrosulfide

As discussed in the foregoing description of refinery unit processes, sour waters are usually generated by these unit processes:

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- Crude oil distillation units, when processing crude oils which contain some dissolved hydrogen sulfide
- Vacuum distillation units, when processing sour crude oils and some cracking occurs in the distillation heater
- Fluid catalytic crackers processing sour gas oils (those containing organic sulfur)
- Thermal crackers, either cokers or visbreakers, processing sour feedstocks
- Hydrocrackers and hydrotreaters, which almost invariably process sour feedstocks
- Gas recovery plants handling sour gases
- Steam crackers processing sour feedstocks

Most refineries segregate and collect all of their sour waters for processing through a sour water stripper[1,5], wherein about 95-99 percent of the hydrogen sulfide and 80-95 percent of the ammonia are removed by distillation. The overhead gas from the stripper, containing hydrogen sulfide and ammonia, may be sent to a refinery's Claus unit for conversion into byproduct sulfur. The stripped water, containing a few ppm of hydrogen sulfide and perhaps 50-200 ppm of ammonia, is then routed through a refinery's wastewater treatment sequence.

Summary

Table 4 summaries the possible wastewaters from the refinery unit processes discussed in this section.

REFINERY CLASSIFICATION

Refineries may be classified in any number of ways. As discussed earlier herein, refineries might be classified on the basis of the endproducts they yield...such as motor fuel refineries, fuel oil refineries, lubricating oil refineries, etc. However, for the purposes of this report, refineries will be classified in terms of their processing complexity as defined by the types of unit processes used in the refineries. In essence, the refinery classifications in this report will be the same as used by the U.S. EPA[6]:

- Category A (Topping Refineries) -- refineries which include atmospheric crude oil distillation and catalytic reforming with or without any other processes (excluding cracking processes).
- Category B (Cracking Refineries) -- refineries which include atmospheric crude oil distillation, catalytic reforming and cracking with or without any other processes (excluding lubricating oil and petrochemical production processes).

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TABLE 4. WASTEWATER SOURCES FROM REFINERY UNIT PROCESSES

Processes	Wastewaters?	Pollutants typically expected in wastewater
Crude oil desalting	yes	Inorganic chlorides, HC, (H_2S, phenols)
Atmospheric distillation	yes	HC, H_2S, (NH_3, phenols)
Vacuum distillation	yes	HC, (NH_3, phenols)
Fluid catalytic cracking	yes	HC, H_2S, NH_3, CN, phenols
Coking (delayed or fluid)	yes	HC, H_2S, NH_3, CN, phenols
Visbreaking	yes	HC, H_2S, NH_3, CN, phenols
Steam cracking (gas oils)	yes	HC, H_2S, NH_3, CN, phenols
Catalytic hydrocracking	yes	H_2S, NH_3, (HC)
Catalytic reforming	no	
Naphtha HDS	yes	H_2S, NH_3, HC, (phenols)
Distillate HDS	yes	H_2S, NH_3, HC, (phenols)
Heavy oil HDS	yes	H_2S, NH_3, HC, (phenols)
Gas recovery plants:		
Unsaturates	yes	H_2S, NH_3, RSH, CN, amine, (HC, phenols)
Saturates	yes	H_2S, NH_3, RSH, amine, (HC)
Merox treaters	yes	NaSH, NaSR, sodium phenolates, (HC)
Alkylation	yes	Sulfuric or hydrofluoric acid or acid salts
Isomerization	no	
Hydrogen synthesis	(yes)	(CO_2, CN, NH_3, amine)
Aromatics extraction	(yes)	(solvents, aromatic HC)
Petrochemicals	(yes)	(various)
Lubricating oil	yes	Solvents and various others
Asphalt	yes	HC, (phenols)
Sulfur recovery	no	

Abbreviations: HC -- hydrocarbon liquids or oils
H_2S -- hydrogen sulfide
NH_3 -- ammonia
CN -- cyanides and thiocyanates
RSH -- mercaptans
NaSR -- sodium mercaptides
NaSH -- sodium hydrosulfide
CO_2 -- carbon dioxide

The pollutants enclosed in ( ) indicate those which may not be present in all cases.

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- Category C (Petrochemical Refineries) -- refineries which include atmospheric crude oil distillation, catalytic reforming, cracking and petrochemical production processes with or without any other processes (excluding lubricating oil production processes).

- Category D (Lubricating Oil Refineries) -- refineries which include atmospheric crude oil distillation processes, catalytic reforming, cracking and lubricating oil production processes with or without any other processes (excluding petrochemical production processes).

- Category E (Integrated Refineries) -- refineries which include atmospheric crude oil distillation, catalytic reforming, cracking, lubricating oil production processes and petrochemical production processes with or without any other processes.

Table 5 lists the various unit processes which are included or may be included within each of the refinery classification categories defined by the EPA. The EPA's classifications are fairly straight-forward except for the definition of petrochemical operations. The EPA's definition includes "first generation" petrochemicals (such as BTX and olefins which are produced directly from refinery intermediate streams) as well as "second generation" petrochemicals (such as cumene and styrene which are produced from the first generation petrochemicals). And the EPA further stipulates that:

- Any production of second-generation petrochemicals constitutes petrochemical operations or processes.

- But production of first-generation petrochemicals must amount to 15 percent or more of refinery production to constitute petrochemical operations.

Thus, a small steam cracker in a large refinery might be classified as a cracker, whereas a large steam cracker in a small refinery might be classified as a petrochemical unit... even though the steam cracker produces first-generation petrochemicals (ethylene and propylene) in either case. The same situation applies to the extraction of BTX from catalytic reformate...it might or might not be classified as a petrochemical unit depending upon its size relative to the refinery size. As footnoted in Table 5, for the purposes of this report, steam crackers and aromatics extraction units are taken to be petrochemical processes on the basis that their output of first-generation petrochemicals exceeds 15 percent of the refinery production. But the readers of this report should understand that such may not always be the case in terms of the EPA's definition.

Topping Refineries (Category A)

Figure 3 is a flow diagram of a typical topping refinery in which:

- The feedstock crude oil is desalted and then distilled in an atmospheric distillation unit.

- The virgin heavy naphtha from the atmospheric distillation unit is hydrode-

TABLE 5. REFINERY CLASSIFICATIONS AS DEFINED BY UNIT PROCESSES IN EACH REFINERY CATEGORY

PROCESSES	CATEGORY A	CATEGORY B	CATEGORY C	CATEGORY D	CATEGORY E
Crude oil distillation:					
Atmospheric	●	●	●	●	●
Vacuum	●	●	●	●	●
Fluid catalytic cracking	x	●	●	●	●
Catalytic hydrocracking	x	●	●	●	●
Delayed coking	x	●	●	●	●
Fluid bed coking	x	●	●	●	●
Visbreaking	x	●	●	●	●
Steam cracking (of gas oils)[a]	●	x	●	x	●
Catalytic reforming	●	●	●	●	●
Naphtha HDS	●	●	●	●	●
Distillate HDS	●	●	●	●	●
Heavy oil HDS	●	●	●	●	●
Gas recovery plants:					
Unsaturates	na	●	●	●	●
Saturates	●	●	●	●	●
Alkylation	na	●	●	●	●
Catalytic polymerization	na	●	●	●	●
Butane isomerization	na	●	●	●	●
Pentane-Hexane isomerization	●	●	●	●	●
Hydrogen synthesis	●	●	●	●	●
Aromatics extraction[a]	●	x	●	x	●
Petrochemicals	●	x	●	x	●
Lubricating oil	●	x	x	●	●
Asphalt	●	●	●	●	●
Sulfur recovery	●	●	●	●	●

● These processes are included or may be included by the category definition

x These processes are excluded by the category definition

na Not applicable for refineries without cracking units

a Defined as petrochemical producing processes for this listing

CATEGORY A -- Topping Refineries
CATEGORY B -- Cracking Refineries
CATEGORY C -- Petrochemical Refineries
CATEGORY D -- Lubricating Oil Refineries
CATEGORY E -- Integrated Refineries

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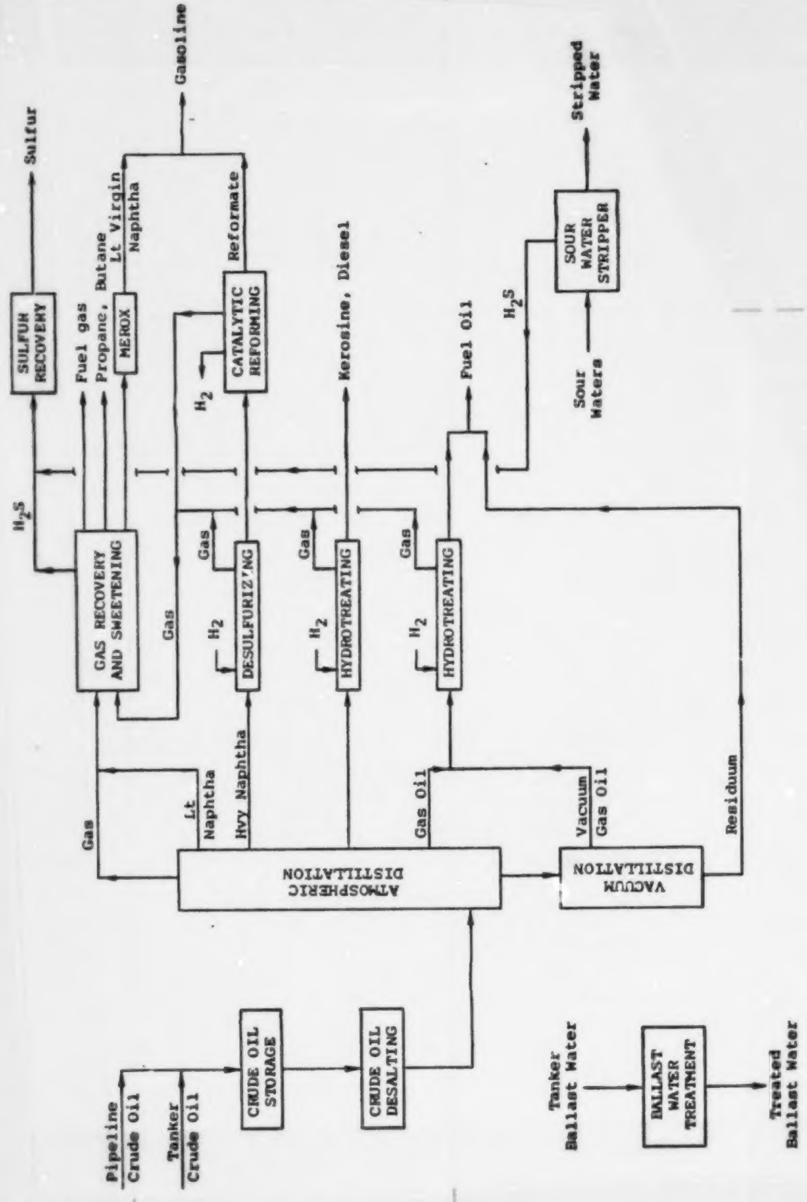
Pipeline Crude Oil
Tanker Crude Oil
CRUDE OIL STORAGE
CRUDE OIL DESALTING
ATMOSPHERIC DISTILLATION
VACUUM DISTILLATION
Gas
Lt Naphtha
Hvy Naphtha
Gas Oil
Vacuum Gas Oil
Residuum
GAS RECOVERY AND SWEETENING
DESULFURIZ'NG
HYDROTREATING
HYDROTREATING
H_2
Gas
H_2S
SULFUR RECOVERY
Sulfur
Fuel gas
Propane, Butane
MEROX
Lt Virgin Naphtha
CATALYTIC REFORMING
Reformate
Gasoline
Kerosine, Diesel
Fuel Oil
SOUR WATER STRIPPER
Sour Waters
Stripped Water
Tanker Ballast Water
BALLAST WATER TREATMENT
Treated Ballast Water

FIGURE 3. An Example of a Category A Refinery (Topping Refinery)

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sulfurized and catalytically reformed to yield a sulfur-free, high-octane gasoline component.

- The virgin kerosine and diesel from the atmospheric distillation unit are hydrotreated for sulfur removal.
- The residual oil from the bottom of the atmospheric distillation unit is vacuum distilled to yield additional gas oil.
- The combined virgin gas oils from the atmospheric and vacuum distillation units are hydrotreated for sulfur removal and then blended with the vacuum distillation residual oil to produce fuel oil.
- Hydrogen for the desulfurizer and hydrotreaters is produced by the reforming unit.
- The various process unit gases are routed through a gas recovery plant to recover sweet refinery fuel gas, propane and butane, LPG, and a light virgin naphtha.
- The light virgin naphtha is Merox treated for removal of mercaptans and then blended with the catalytic reformate to produce the refinery's endproduct gasoline.
- The hydrogen sulfide from the amine scrubbing in the gas recovery plant and from the refinery's sour water stripper is converted into byproduct sulfur in a Claus sulfur recovery unit.

The topping refinery depicted in Figure 3 is a fairly simple one. As shown in Table 5, topping refineries may be quite a bit more complex. For example, if the catalytic reformer hydrogen yield is not sufficient to supply the hydrotreaters, then a hydrogen synthesis unit would be required. In some cases, the light virgin naphtha (pentanes and hexanes) may be catalytically isomerized for octane rating improvement. Topping refineries may also include aromatics (BTX) extraction from the catalytic reformate, lubricating oil production and asphalt production. Thus, Figure 3 depicts only one of many processing configurations that could be classified as a topping refinery. However, it contains the primary or fundamental process units typical of most topping refineries.

Cracking Refineries (Category B)

Figure 4 is a flow diagram of a cracking refinery in which:

- The desalted crude oil feedstock is distilled (by atmospheric and vacuum distillation) to yield gas, virgin naphthas, virgin kerosine and diesel, and virgin gas oils.
- The virgin heavy naphtha is hydrodesulfurized and catalytically reformed. The sulfur-free, high-octane catalytic reformate is sent to endproduct gasoline blending.

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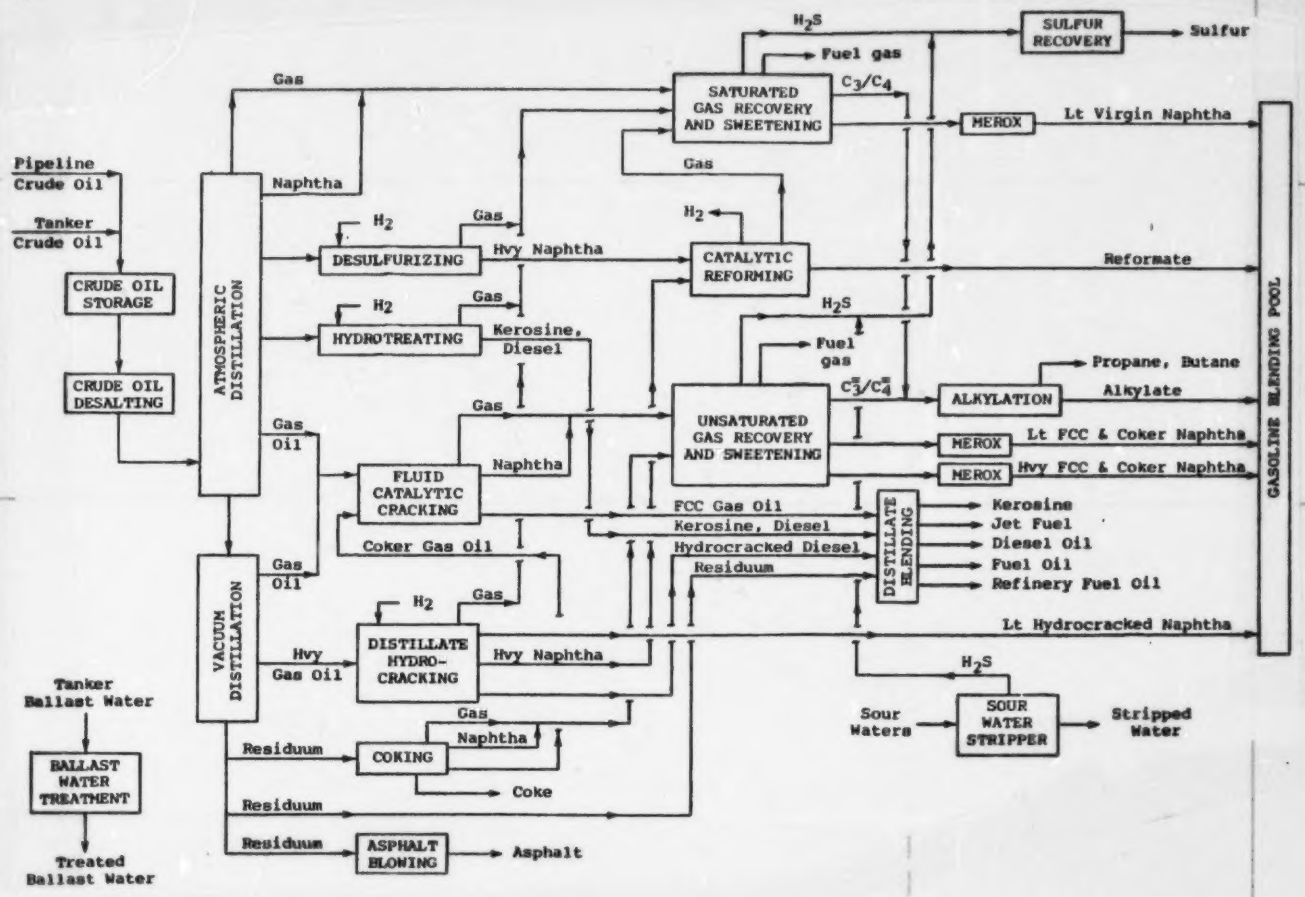
Pipeline Crude Oil
Tanker Crude Oil
CRUDE OIL STORAGE
CRUDE OIL DESALTING
ATMOSPHERIC DISTILLATION
VACUUM DISTILLATION
Gas
Naphtha
Gas Oil
Gas Oil
Hvy Gas Oil
Residuum
Residuum
Residuum
H_2
DESULFURIZING
Gas
Hvy Naphtha
H_2
HYDROTREATING
Gas
Kerosine, Diesel
FLUID CATALYTIC CRACKING
Gas
Naphtha
Coker Gas Oil
H_2
DISTILLATE HYDRO-CRACKING
Gas
Hvy Naphtha
COKING
Gas
Naphtha
Coke
ASPHALT BLOWING
Asphalt
SATURATED GAS RECOVERY AND SWEETENING
H_2S
Fuel gas
C_3/C_4
Gas
CATALYTIC REFORMING
H_2
UNSATURATED GAS RECOVERY AND SWEETENING
H_2S
Fuel gas
$C_3^=/C_4^=$
FCC Gas Oil
Kerosine, Diesel
Hydrocracked Diesel
Residuum
SULFUR RECOVERY
Sulfur
MEROX
Lt Virgin Naphtha
Reformate
ALKYLATION
Propane, Butane
Alkylate
MEROX
Lt FCC & Coker Naphtha
MEROX
Hvy FCC & Coker Naphtha
DISTILLATE BLENDING
Kerosine
Jet Fuel
Diesel Oil
Fuel Oil
Refinery Fuel Oil
Lt Hydrocracked Naphtha
GASOLINE BLENDING POOL
H_2S
Sour Waters
SOUR WATER STRIPPER
Stripped Water
Tanker Ballast Water
BALLAST WATER TREATMENT
Treated Ballast Water

FIGURE 4. An Example of a Category B Refinery (Cracking Refinery)

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- The virgin kerosine and diesel are hydrotreated for sulfur removal.
- To minimize fuel oil production and maximize gasoline production, the light virgin gas oils are cracked in a fluid catalytic cracking unit and the heavy virgin gas oil is catalytically hydrocracked.
- Part of the vacuum distillation residual oil is coked (to further maximize gasoline production), part is air-blown to produce asphalt and the remainder is blended into fuel oil.
- To maximize gasoline production even further, the gas oil yielded from the coker is fed to the fluid catalytic cracking unit for cracking.
- The heavy naphtha from the hydrocracker is sent to the catalytic reformer for octane upgrading.
- The gases and light naphthas from the fluid catalytic cracking unit and the coker (with a high content of unsaturated olefinic components) are routed through an unsaturate gas recovery plant.
- The isoparaffinic, light hydrocracked naphtha, which has a very good octane rating, is sent directly to endproduct gasoline blending.
- The other gases and light naphthas from the atmospheric distillation unit, the catalytic reformer, the hydrocracker and the hydrotreaters (all of which are primarily saturated paraffins) are routed through a saturate gas recovery plant.
- The naphthas recovered from the two gas recovery plants are Merox treated for mercaptan removal and then sent to endproduct gasoline blending.
- An alkylation unit produces a very high-octane gasoline component by combining isobutane in the saturate gas plant C3/C4 cut with the propylene and butylenes in the unsaturate gas plant $C3^{=}/C4^{=}$ cut.
- The refinery's endproduct gasolines are produced by blending:

  Light virgin naphtha, catalytic reformate, alkylate, light and heavy fluid catalytic cracking and coker naphthas, and light hydrocracked naphtha.
- The refinery's distillate oils (virgin kerosine and diesel, fluid catalytic cracking gas oil and hydrocracked diesel) are blended to produce kerosine, jet fuel and diesel oil. Some of the heavier distillate oils are blended with vacuum residual oil to produce endproduct fuel oil as well as refinery fuel oil.
- Hydrogen sulfide from the amine scrubbing in the gas recovery plants and from the sour water stripper is converted to byproduct sulfur in a Claus sulfur recovery unit.

A comparison of Figures 3 and 4 illustrates that a cracking refinery is very much more complex than a topping refinery. And, in many cases, it may be even more complex.

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For example:

- The butylenes fed to alkylation often require catalytic hydrogenation to convert butadiene into butylenes.
- If the isobutane in the saturate gas plant, C3/C4, is not sufficient to alkylate all of the refinery's propylene and butylene, then a butane isomerization unit is often added to convert the normal butane into isobutane.
- If the hydrogen yielded by the reformer is insufficient to supply the hydrotreaters and the hydrocracker (which has a very high hydrogen demand), then a hydrogen synthesis plant would be required.
- In some cases, a cracking refinery alkylates its butylenes but catalytically polymerizes its propylene.
- In some cases, the light virgin naphtha (pentanes and hexanes) may be catalytically isomerized for octane-rating improvement.

The cracking refinery depicted in Figure 4 has both fluid catalytic cracking and catalytic hydrocracking. That is not always the case. Some cracking refineries have only fluid catalytic crackers and some have only hydrocrackers. Other cracking refineries have no coker, and yet others may have visbreakers (thermal crackers). Thus, a cracking refinery may also be considerably less complex than the one shown in Figure 4 ...but in general they are still much more complex than a topping refinery.

Petrochemical Refinery (Category C)

Figure 5 is a flow diagram of a petrochemical refinery. It is identical with the cracking refinery in Figure 4 except for these additional process units:

- An aromatics production unit which extracts BTX from a portion of the refinery's catalytic reformate.
- Second-generation petrochemical production processes:
  - (a) Ethylbenzene production by the catalytic reaction of benzene and ethylene.
  - (b) Styrene production by the catalytic dehydrogenation of ethylbenzene.
  - (c) Cumene production by the catalytic reaction of benzene and propylene.

  The ethylene and propylene feedstocks ($C2^{=}/C3^{=}$) for the second-generation petrochemical units are obtained from the refinery unsaturate gas recovery plant. The benzene feedstock is obtained from the BTX extraction unit.

In terms of producing motor fuels, distillate oils and fuel oil, the petrochemical refinery in Figure 5 uses the same configuration of process units as the cracking refinery in Figure 4. As with the cracking refinery, there may be many other petrochemical refinery

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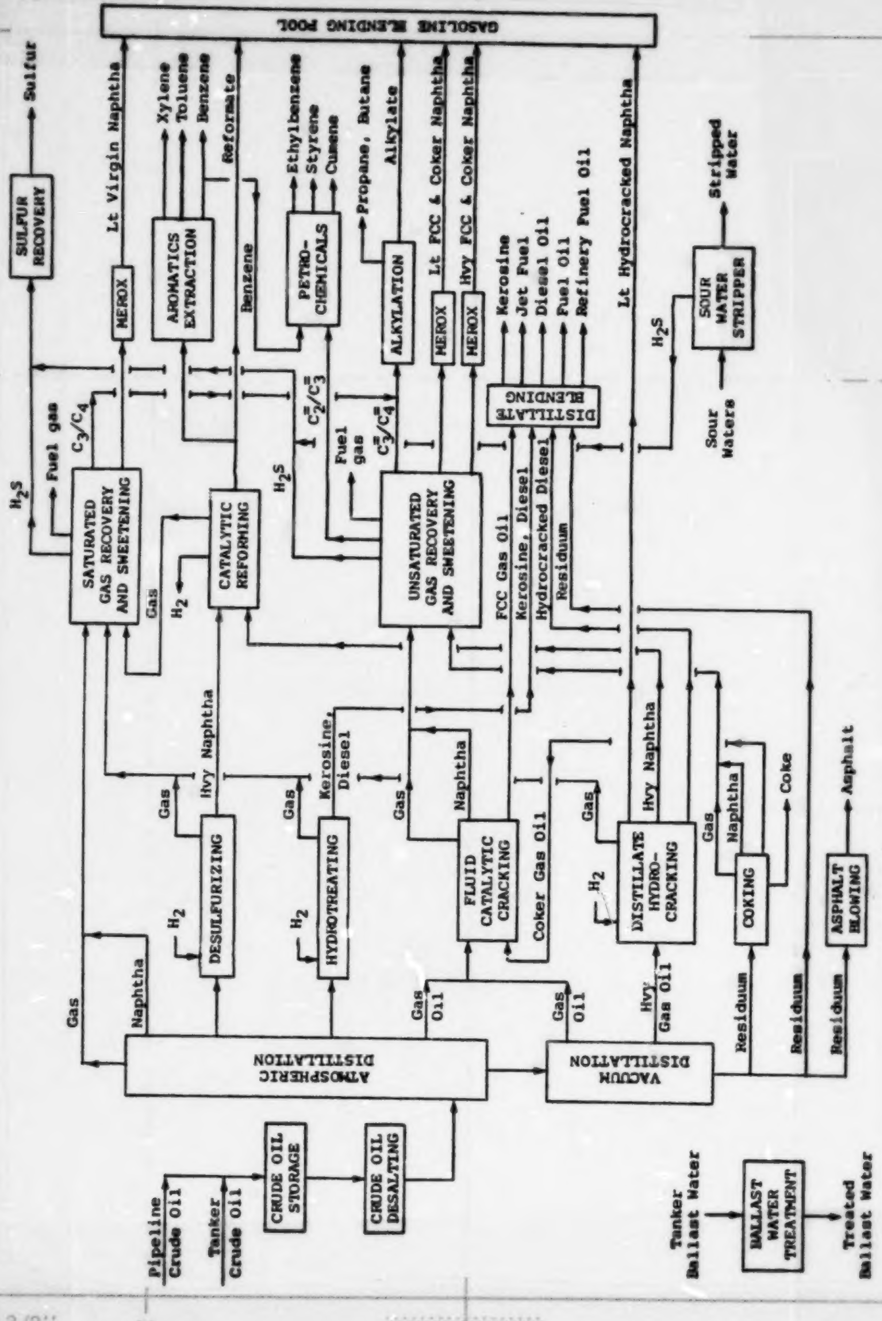
GASOLINE BLENDING POOL
SULFUR RECOVERY
Sulfur
H2S
Fuel gas
C3/C4
SATURATED GAS RECOVERY AND SWEETENING
MEROX
Lt Virgin Naphtha
AROMATICS EXTRACTION
Xylene
Toluene
Benzene
Reformate
CATALYTIC REFORMING
H2
Gas
Benzene
PETRO-CHEMICALS
Ethylbenzene
Styrene
Cumene
C2=/C3=
Propane, Butane
ALKYLATION
Alkylate
Fuel gas
C3=/C4=
UNSATURATED GAS RECOVERY AND SWEETENING
MEROX
Lt FCC & Coker Naphtha
MEROX
Hvy FCC & Coker Naphtha
DISTILLATE BLENDING
Kerosine
Jet Fuel
Diesel Oil
Fuel Oil
Refinery Fuel Oil
FCC Gas Oil
Kerosine, Diesel
Hydrocracked Diesel
Residuum
Lt Hydrocracked Naphtha
SOUR WATER STRIPPER
Stripped Water
Sour Waters
Gas
Naphtha
Hvy Naphtha
DESULFURIZING
Kerosine, Diesel
HYDROTREATING
Naphtha
FLUID CATALYTIC CRACKING
Coker Gas Oil
DISTILLATE HYDRO-CRACKING
Hvy Naphtha
COKING
Coke
ASPHALT BLOWING
Asphalt
Gas Oil
Hvy Gas Oil
Residuum
ATMOSPHERIC DISTILLATION
VACUUM DISTILLATION
Pipeline Crude Oil
Tanker Crude Oil
CRUDE OIL STORAGE
CRUDE OIL DESALTING
Tanker Ballast Water
BALLAST WATER TREATMENT
Treated Ballast Water

FIGURE 5. An Example of a Category C Refinery (Petrochemical Refinery)

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configurations which are more complex:

- A steam cracker might be added, using part of the refinery's virgin gas oil as feedstock, to produce ethylene, propylene, butadiene and aromatics as well as byproduct gasoline and fuel oil.
- Cyclohexane might be produced by the catalytic hydrogenation of benzene.
- The same possible variants as discussed for the cracking refinery apply to the petrochemical refinery.

Thus, Figure 5 depicts only one of the many processing configurations that could be classified as a petrochemical refinery.

Lubricating Oil Refinery (Category D)

Figure 6 is a flow diagram of a lubricating oil (lube oil) refinery. It is identical with the cracking refinery in Figure 4 with the exception that it includes processing units for producing a range of lubricating oils.

The feedstocks for the lubricating oil processes are gas oil and residual oil obtained from the vacuum distillation unit. The various processes that may be included in the lubricating oil unit are:

- SDA of the vacuum residual oil feedstock.
- Solvent extraction of aromatics and resins from the feedstocks for improving the viscosity index of the endproduct lubricating oils.
- Solvent extraction of waxes from the feedstocks for lowering the pour point of the endproduct lubricating oils.

Figure 6 depicts only one of the many processing configurations that could be classified as lubricating oil refineries. All of the possible variants discussed for a topping refinery and for a cracking refinery apply to a lubricating oil refinery as well.

Integrated Refinery (Category E)

Figure 7 is a flow diagram of an integrated or "combination" refinery, which is one that combines all of the elements of cracking, petrochemical and lubricating oil refineries.

As with the other refinery categories, Figure 7 depicts only one of the very many processing configurations that could be classified as integrated refineries.

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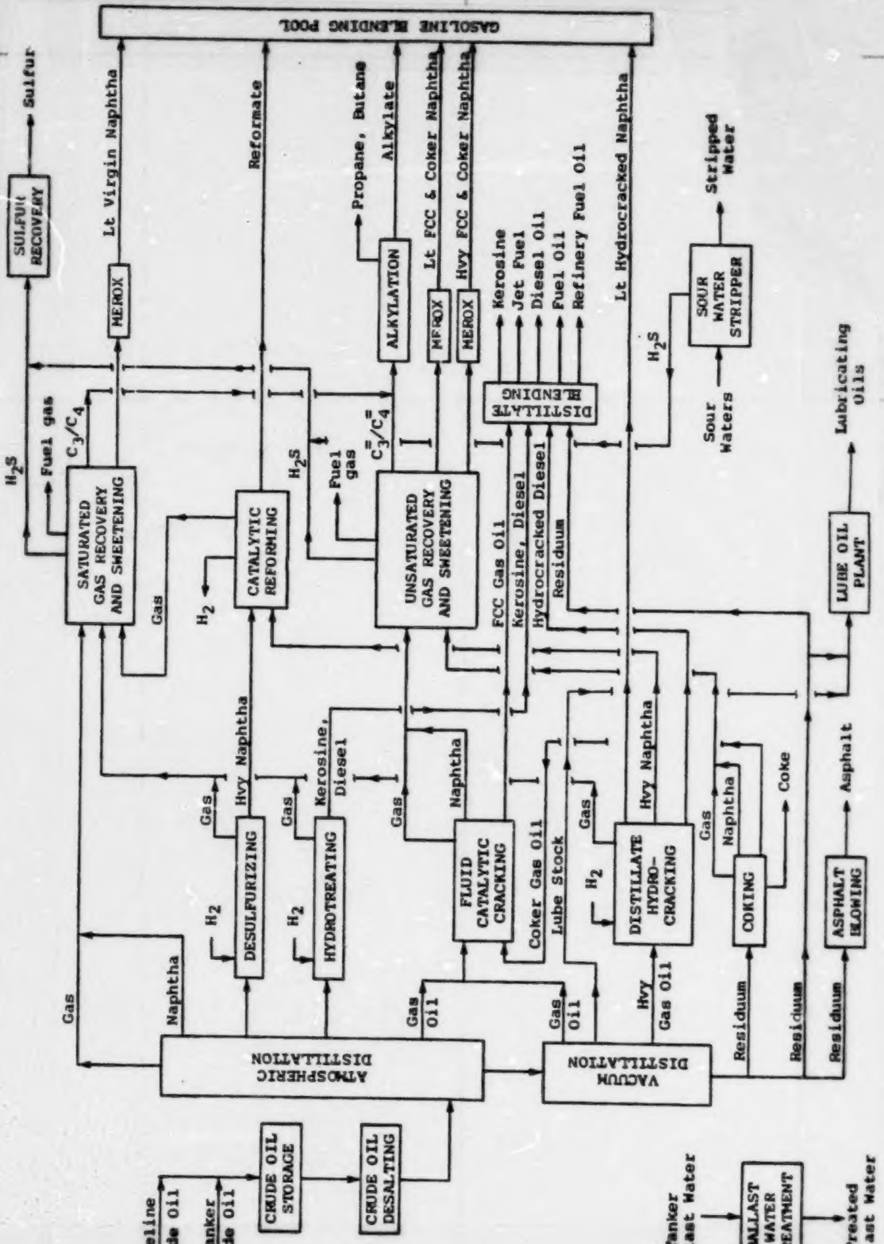
GASOLINE BLENDING POOL
SULFUR RECOVERY
Sulfur
MEROX
Lt Virgin Naphtha
Reformate
Propane, Butane
Alkylate
ALKYLATION
Lt FCC & Coker Naphtha
MEROX
Hvy FCC & Coker Naphtha
MEROX
Kerosine
Jet Fuel
Diesel Oil
Fuel Oil
Refinery Fuel Oil
DISTILLATE BLENDING
Lt Hydrocracked Naphtha
H_2S
SOUR WATER STRIPPER
Stripped Water
Sour Waters
Lubricating Oils
LUBE OIL PLANT
H_2S
Fuel gas
C_3/C_4
SATURATED GAS RECOVERY AND SWEETENING
Gas
CATALYTIC REFORMING
H_2
H_2S
Fuel gas
$C_3^=/C_4^=$
UNSATURATED GAS RECOVERY AND SWEETENING
FCC Gas Oil
Kerosine, Diesel
Hydrocracked Diesel
Residuum
Hvy Naphtha
Gas
Kerosine, Diesel
Gas
Gas
Naphtha
DESULFURIZING
H_2
HYDROTREATING
H_2
FLUID CATALYTIC CRACKING
Coker Gas Oil
Lube Stock
Gas
Hvy Naphtha
H_2
DISTILLATE HYDRO-CRACKING
Gas
Naphtha
COKING
Coke
Asphalt
ASPHALT BLOWING
Gas
Naphtha
Gas Oil
Gas Oil
Hvy Gas Oil
Residuum
Residuum
Residuum
ATMOSPHERIC DISTILLATION
VACUUM DISTILLATION
Pipeline Crude Oil
Tanker Crude Oil
CRUDE OIL STORAGE
CRUDE OIL DESALTING
Tanker Ballast Water
BALLAST WATER TREATMENT
Treated Ballast Water

FIGURE 6. An Example of a Category D Refinery (Lube Oil Refinery)

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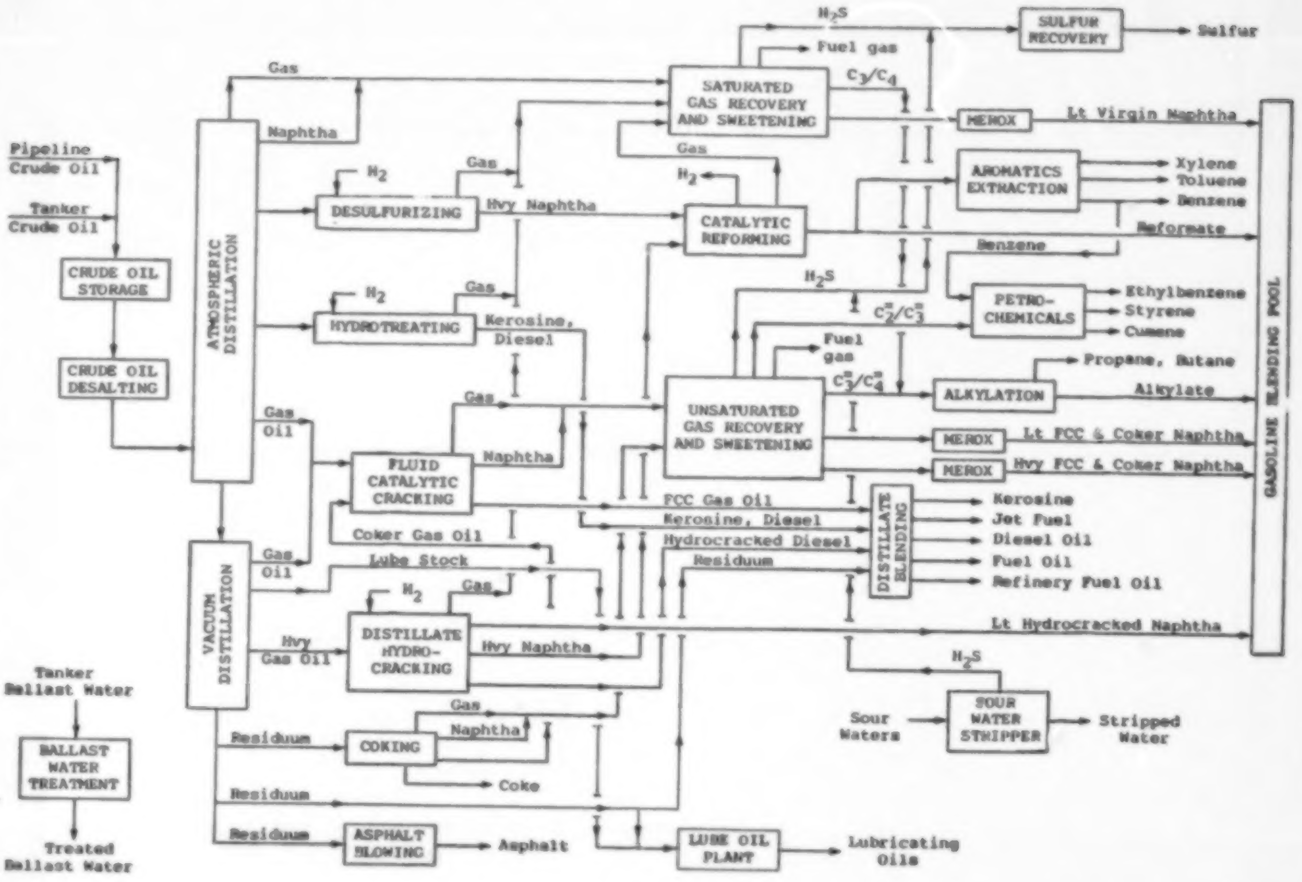
Pipeline Crude Oil
Tanker Crude Oil
CRUDE OIL STORAGE
CRUDE OIL DESALTING
ATMOSPHERIC DISTILLATION
VACUUM DISTILLATION
Gas
Naphtha
Gas Oil
Hvy Gas Oil
Residuum
H2
DESULFURIZING
Hvy Naphtha
HYDROTREATING
Kerosine, Diesel
FLUID CATALYTIC CRACKING
Coker Gas Oil
Lube Stock
DISTILLATE HYDRO-CRACKING
COKING
Coke
ASPHALT BLOWING
Asphalt
LUBE OIL PLANT
Lubricating Oils
SATURATED GAS RECOVERY AND SWEETENING
H2S
Fuel gas
C3/C4
SULFUR RECOVERY
Sulfur
MEROX
Lt Virgin Naphtha
CATALYTIC REFORMING
AROMATICS EXTRACTION
Xylene
Toluene
Benzene
Reformate
PETRO-CHEMICALS
Ethylbenzene
Styrene
Cumene
C2=/C3=
C3=/C4=
UNSATURATED GAS RECOVERY AND SWEETENING
ALKYLATION
Propane, Butane
Alkylate
Lt FCC & Coker Naphtha
Hvy FCC & Coker Naphtha
FCC Gas Oil
Kerosine, Diesel
Hydrocracked Diesel
DISTILLATE BLENDING
Kerosine
Jet Fuel
Diesel Oil
Fuel Oil
Refinery Fuel Oil
Lt Hydrocracked Naphtha
GASOLINE BLENDING POOL
Sour Waters
SOUR WATER STRIPPER
Stripped Water
Tanker Ballast Water
BALLAST WATER TREATMENT
Treated Ballast Water

FIGURE 7. An Example of a Category E Refinery (Integrated Refinery)

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REFINERY WASTEWATERS

Thus far, this section has dealt primarily with the unit processes used in petroleum refineries and with the wastewaters generated by the individual processes (as summarized in Table 4. However, there are a number of non-process wastewater sources in most refineries, and the purpose of this section is to discuss all of the wastewaters that may be encountered in refineries including non-process as well as process sources.

Wastewater Sources

Figure 8 depicts all of the wastewater sources typically encountered in petroleum refining:

- Wastewaters from process units, which includes:
  - (a) Sour waters (process steam condensates and wash waters) as previously discussed and summarized in Table 4.
  - (b) Miscellaneous solvents and chemical wastes (also summarized in Table 4) as well as drips and drains from valves, pumps, sample taps, etc.
  - (c) Rainwater runoff from process unit areas.
- Drainage from tank farms (storage tank diked areas).
- Ballast water withdrawn from the cargo holds of incoming empty tankers at those refineries which ship some or all of their endproducts by tankers.
- Cooling tower blowdown at those refineries which use circulating cooling water systems with evaporative cooling towers.
- The wastewater brines from the treatment (softening and/or demineralizing) of the refinery's intake water supply.
- Blowdown from the steam-generating boilers in a refinery, which includes utility steam boilers as well as process heat recovery steam generators (waste heat boilers).
- Sanitary water effluents (from wash room and toilet facilities).
- Clean rainwater runoff from non-process areas such as roads, parking lots, utility plant areas, etc.
- Wastewaters from the refinery laboratory (not shown in Figure 8 for the sake of simplicity).

It must be emphasized that some refineries may include all of the wastewater sources shown in Figure 8, but other refineries may not. For example, many refineries do not ship products by tanker and hence would not have ballast water to handle. As another example, some refineries utilize once-through cooling water systems rather than circulating cooling water systems and therefore would not have any cooling tower blowdown.

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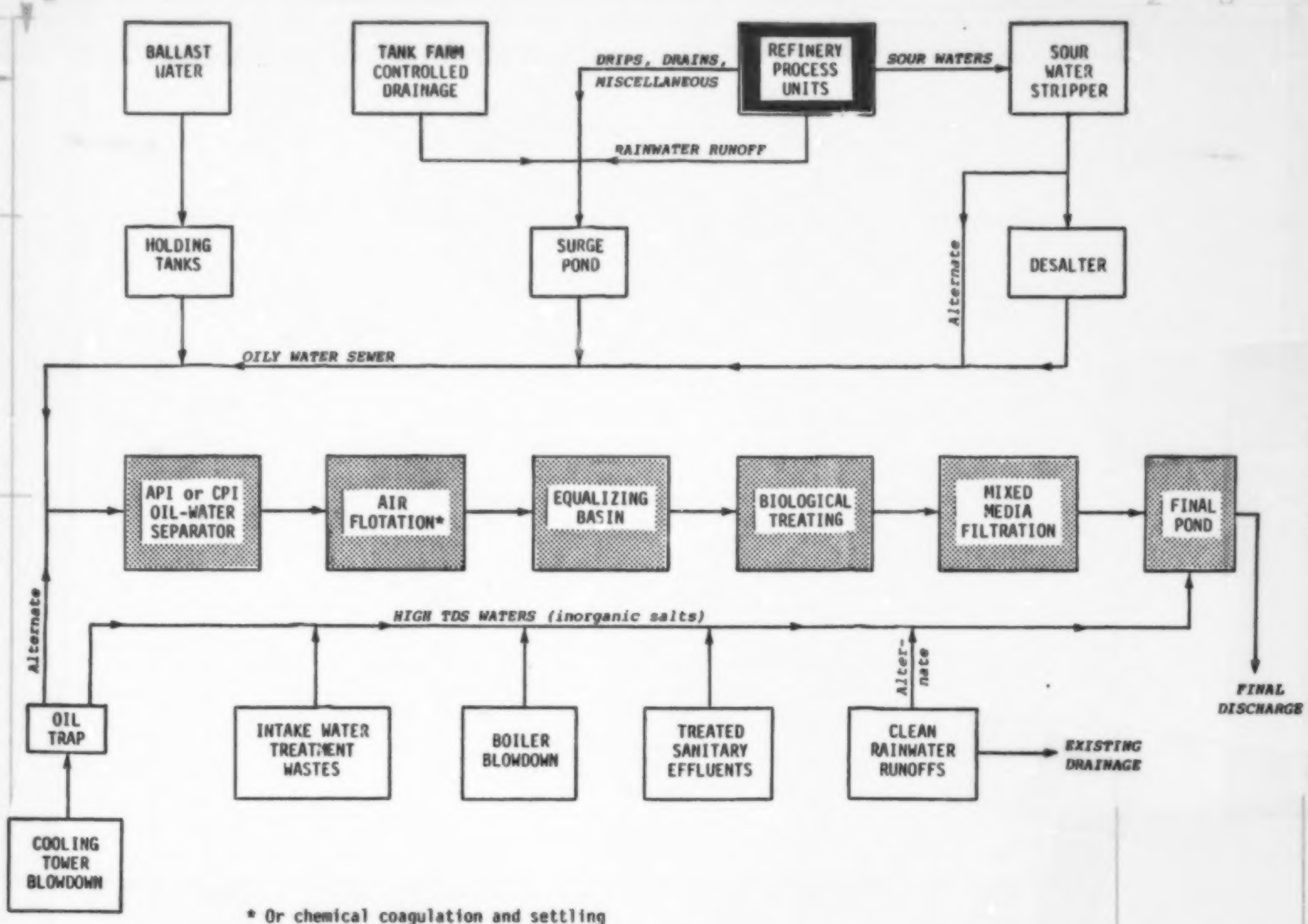
BALLAST WATER
TANK FARM CONTROLLED DRAINAGE
DRIPS, DRAINS, MISCELLANEOUS
REFINERY PROCESS UNITS
SOUR WATERS
SOUR WATER STRIPPER
RAINWATER RUNOFF
HOLDING TANKS
SURGE POND
Alternate
DESALTER
OILY WATER SEWER
API or CPI OIL-WATER SEPARATOR
AIR FLOTATION*
EQUALIZING BASIN
BIOLOGICAL TREATING
MIXED MEDIA FILTRATION
FINAL POND
Alternate
HIGH TDS WATERS (inorganic salts)
Alter-nate
FINAL DISCHARGE
OIL TRAP
INTAKE WATER TREATMENT WASTES
BOILER BLOWDOWN
TREATED SANITARY EFFLUENTS
CLEAN RAINWATER RUNOFFS
EXISTING DRAINAGE
COOLING TOWER BLOWDOWN

* Or chemical coagulation and settling

FIGURE 8. Wastewater sources and wastewater management in a refinery.

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Figure 8 also depicts a wastewater management or treatment sequence which includes:

- Primary removal of oil and suspended solids from the oily water sewer flow, using a gravimetric oil-water separator of either the API design or the corrugated plate interceptor (CPI) type.
- Secondary removal of oil and suspended solids, using either air flotation or chemical coagulation and settling.
- An equalizing basin which provides intermediate storage and mixing of the incoming wastewater to "smooth out" any fluctuations in wastewater flow and composition so as to obtain a uniform feed to the biological treatment step.
- Biological treatment which may utilize:
  - (a) An aerated lagoon system
  - (b) A trickle filter process
  - (c) An activated sludge process
  - (d) Or various combinations of aerated lagoons, trickle filters and activated sludge units.
- Mixed media filtration for the final removal of suspended biological solids.
- A final storage pond which provides for testing and quality control before final discharge of the treated effluent.
- A separate sewer for non-oily wastewater, which contains a relatively high concentration of total dissolved solids (TDS) primarily in the form of inorganic salts. Such non-oily, high TDS wastewaters may be routed directly to the final pond as shown in Figure 8.

The total wastewater flow generated by petroleum refining varies very widely from one refinery to another. There are many factors that influence the wastewater flow from any given refinery, some of which are:

- The refinery's processing configuration as defined by the refinery categories discussed herein.
- The annual rainfall at the refinery's geographical location.
- The type of cooling water system used in the refinery (that is, whether once-through or circulating).
- Whether or not the refinery must handle tanker ballast water.
- The age of the refinery and the degree of good "housekeeping" practiced within the refinery.
- The degree of air-cooling and of wastewater reuse so as to minimize the overall water demand of the refinery.

Based upon data obtained in 1972 from 94 U.S. refineries (each with less than 3 percent of their cooling needs provided by once-through cooling water), the EPA derived these median, dry-weather wastewater flows[6]:

TABLE 6. MEDIAN DRY-WEATHER WASTEWATER FLOWS

Refinery Category	Median wastewater flow (gallons of wastewater/barrel of crude oil)
Topping (Category A)	20
Cracking (Category B)	25
Petrochemical (Category C)	30
Lubricating Oil (Category D)	45
Integrated (Category E)	48

Translated to a refinery processing 100,000 barrels per day of crude oil, the above median wastewater flows range from 1,390 gpm (Category A) to 3,330 gpm (Category E). It must be emphasized that the range of extremes (lowest to highest) was very much broader than the above range of median flows. In any event, these data may provide the reader with a perspective as to the wastewater flow rates encountered in petroleum refineries.

Wastewater Pollutants

Refineries generate a spectrum of wastewater pollutants which includes inorganic salts, hydrocarbon oils, suspended solids, ammonia, sulfides, phenols, mercaptans, cyanides, solvents, heavy metals, etc. To discuss each and every specific pollutant or to classify those which might be considered "hazardous" or "toxic" is beyond the scope of this refinery characterization section. Accordingly, this section is limited to a discussion of the major pollutants or pollutant parameters which have generally been used in the petroleum refining industry to characterize the level of pollutants in refinery wastewater streams:

BOD_5	A parameter which measures the oxygen consumed by the biological oxidation of wastewater pollutants over a 5-day period, commonly called the 5-day biological oxygen demand.
COD	A parameter which measures the oxygen required to chemically oxidize wastewater pollutants using a chemical oxidant and a specific reaction time, commonly called the chemical oxygen demand. There are many different COD measurement methods, and the most common one in the United States uses a dichromate oxidant with a 2-hour reaction time. There is no generalized correlation between the BOD_5 and the COD parameters.

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TOC	A parameter which measures the amount of organic carbon present in a wastewater, commonly called the total organic carbon. There is no reliable, generalized correlation between the BOD_5, COD and TOC parameters. The TOC measurement can be made by an automated, on-line analyzer which provides a rapid determination of organic carbon levels in wastewaters. For specific wastewaters in specific refineries, TOC may be correlated with BOD_5 and COD to provide a continuous indication of the biological and chemical oxygen demand of the wastewater...as long as the operating conditions in the refineries remain within the range for which the TOC was correlated with BOD_5 and COD.
Suspended Solids	The suspended solids content of a wastewater includes organic solids (tar, grease, fibers, hair, sawdust, etc.) and inorganic solids such as sand, silt and clay.
Oil	The oil content of a wastewater includes any oil or grease which is extractable by a specific solvent, usually Freon.
Ammonia	The ammonia content of a wastewater includes free or dissolved ammonia as well as combined ammonia such as in ammonium hydrosulfide. It is usually reported as ammonia nitrogen (NH_3-N), which is the nitrogen fraction of the ammonia amounting to 82 weight percent of the ammonia.
Phenols	The phenols content of a wastewater includes phenol, cresols and xylenols as well as perhaps other phenolic species.
Sulfides	The sulfide content of a wastewater includes free or dissolved hydrogen sulfide as well as combined sulfide such as in ammonium hydrosulfide or in sodium hydrosulfide.
Total Chromium	The total chromium content of a wastewater includes trivalent and hexavalent chromium.

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Many if not all of the laboratory test methods for measuring the above pollutants and pollutant parameters have problems from interfering substances and have varying degrees of repeatability (in the same laboratory by the same analyst on the same sample) as well as varying degrees of reproducibility (by different laboratories or different analysts on the same sample). This makes it quite difficult to obtain meaningful pollutant data comparisons from one refinery to another even when using specified or standardized test methods. In fact, it is often difficult to obtain meaningful comparisons of pollutant data from one wastewater stream to another within the same refinery.

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Each of the above pollutants and pollutant parameters are discussed below in terms of the refinery wastewater sources (depicted in Figure 8) in which those pollutants can normally be expected to be present.

5-day BOD--

Most of the sour wastewaters from the normal operation of refinery process units (see Figure 8) contain biodegradable pollutants and have a significant 5-day BOD. As shown in Table 4, almost all refinery unit processes generate wastes containing oils, solvents and other substances, all of which are biodegradable. Since the process unit areas are usually paved and graded to drain into the oily water sewer, the rainwater run-off and miscellaneous drains and drips from those process areas contain biodegradable pollutants and also have a significant 5-day BOD (although perhaps somewhat lower than the 5-day BOD of the operational sour wastewaters).

After stripping the sour waters for hydrogen sulfide and ammonia removal, the stripped waters are normally routed through a crude oil desalter. The crude oil absorbs and removes a good part of the phenols that may be present in the stripped waters[1]. However, the oily and salt-laden effluent water from the desalter to the oily water sewer has a 5-day BOD which may range from 70 to 600 ppm[1].

The oily water drainage from the storage tank farm has a significant 5-day BOD, as does the oily ballast water removed from tankers arriving to be loaded with outgoing refinery products.

The blowdown from cooling towers in cooling water systems which are in good physical condition do not usually contain any oils or other pollutants that create a 5-day BOD. However, in older systems which may have leaks in their water-cooled process heat exchangers, the cooling tower blowdown may contain a significant amount of oil which creates a significant 5-day BOD.

In summary, the probable wastewater sources of 5-day BOD are these:

- The operational sour or phenolic or oily wastewaters from the refinery unit processes.
- The rainwater runoff and miscellaneous drips and drains from the refinery unit processes.
- The oily ballast water in those refineries shipping products by tanker.
- The oily brine effluent from crude oil desalters.
- The oily drainage water from storage tanks and from their diked enclosures.
- The cooling tower blowdown from refineries in which there are significant leaks in the water-cooled process heat exchangers.

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COD--

In general, the wastewater sources of COD in a refinery are identical with the 5-day BOD sources discussed just above. Although there is no generalized correlation between COD and 5-day BOD, the level of COD in refinery wastewaters is typically higher than the level of 5-day BOD by a factor of 1.5-2.0 or more.

TOC--

In general, the wastewater sources of TOC in a refinery are also identical with the 5-day BOD sources. There is no generalized correlation between TOC, COD and 5-day BOD and the level of TOC in refinery wastewaters may be higher or lower than the level of 5-day BOD (but TOC is generally lower than COD).

Oil--

The sources of oily wastewaters in a refinery are identical with those for 5-day BOD, and that is all of the sources shown as routed into the oily water sewer in Figure 8.

Suspended Solids--

All of the wastewaters in a refinery, whether oily or non-oily, are sources of suspended solids. That includes the wastewaters which are not routed into the oily water sewers such as cooling tower blowdown, boiler blowdown, intake water treatment wastes, treated sanitary wastes and clean rainwater runoff. However, the sources of oily suspended solids are the same as for oil or for 5-day BOD.

TDS--

TDS in refinery wastewaters consist mostly of inorganic salts and their major sources are:

- Cooling tower blowdown
- Boiler blowdown
- Intake water treatment wastes

Most refinery cooling towers operate within the range of two to seven cycles of concentration due to the evaporation required to remove the heat absorbed by the circulating cooling water. Thus, the cooling tower acts like an evaporative concentrator and the concentration of inorganic salts in the tower blowdown is two to seven times the concentration of the salts entering the tower in the treated makeup water (which replaces the evaporated water and the blowdown water).

Boiler blowdowns also contain high levels of TDS due to the evaporation of water to generate steam, which leaves behind a highly concentrated inorganic salt solution. The level of TDS in a boiler blowdown depends upon the degree to which the boiler feedwater has been softened or demineralized, and upon the pressure level of the steam generated which determines the amount of blowdown needed to maintain a tolerable level of dissolved salts. In general, the TDS in refinery boiler blowdowns ranges from 1,000 ppm in high pressure steam boilers to 4,000 ppm in low pressure boilers.

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The degree of intake water treatment required and whether the treatment is softening or demineralizing depends largely upon the composition of the intake water supply and upon the steam generation pressure levels in a refinery. In any event, the minerals or salts removed by the intake water treatment generate a high TDS wastewater effluent or brine. The level of TDS in those wastes depends upon the specific treatment unit design and the specific treatment requirements of each refinery.

Ammonia and Sulfides--

As discussed earlier, sour wastewaters are those which contain either dissolved hydrogen sulfide or ammonia and hydrogen sulfide combined in the form of ammonium hydrosulfide. All of the sour wastewaters are derived from the unit processes within a refinery and are usually routed through a sour water stripped (see Figure 8). The stripper removes as much as 99 percent of the hydrogen sulfide and perhaps 80-95 percent of the ammonia. Thus, the stripped sour water routed to the oily water sewer (or reused in the crude oil desalter) normally has only a few ppm of hydrogen sulfide and perhaps 50-200 ppm of ammonia.

Spent caustic solutions from Merox and other treating units (used to scrub refinery liquids for removal of hydrogen sulfide and mercaptans) are also sources of sulfidic wastewaters. Stripping of spent caustics without prior neutralization is largely ineffective in terms of removing hydrogen sulfide. The options for spent caustic disposal are:

- Neutralization followed by stripping prior to routing into the oily water sewer.
- Incineration in a fluidized bed incinerator.
- Deep well disposal in a suitable underground geological strata.
- Offseit disposal by contract with commercial disposal firms.

Phenols--

As discussed in the introduction, most of the phenols appearing in refinery wastewaters are generated by the thermal cracking and fluid catalytic cracking processes used in refineries. Thus, the sour wastewaters from the refinery process units contain significant levels of phenols (especially if the refinery includes cracking processes). Stripping of the sour water may remove about 20-30 percent of the phenols. If the stripped water is then reused in a crude oil desalter, a good part of the phenols remaining in the stripped water will be removed by absorption into the crude oil.

Phenolic spent caustics are those which have been used to scrub cracked naphthas and heavier liquids within the refinery. If the phenolic spent caustics are neutralized, the phenols may be removed and recovered as saleable byproduct[1]. The disposal options for the phenolic spent caustics are the same as for the sulfidic spent caustics discussed just above.

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Total Chromium--

Organic and inorganic chromates are used as corrosion inhibitors in the large majority of refinery cooling water systems, especially in circulating systems with evaporative cooling towers. Thus, the major source of chromium in refinery wastewaters is the blowdown from cooling towers.

SUMMARY AND PERSPECTIVE

All of the wastewater sources (process and non-process) typically encountered in petroleum refineries have been discussed and explained in this section. Those sources and their routing through a typical wastewater management or treatment sequence have been depicted in Figure 8. To provide a perspective, Table 6 presents EPA data on the median, overall dry-weather wastewater flows from each of the EPA's five refinery categories. Those flows ranged from 20 to 48 gallons of wastewater per barrel of crude oil processed.

The pollutants and pollutant parameters commonly used to characterize refinery wastewaters have been defined and discussed in this section. Then each of those pollutants and pollutant parameters have been discussed in terms of identifying the specific wastewater sources in which they can normally be expected to appear.

As a final order-of-magnitude perspective, Table 7 presents data derived by the EPA as to the median pollutant loads (and their equivalent wastewater pollutant concentrations) from each of the EPA's five refinery categories. Excluding the category of topping refineries, the median, overall refinery wastewater pollutant concentrations in Table 7 may be summarized as:

5-day BOD	120-240 ppm
COD	290-650 ppm
TOC	70-210 ppm
Suspended Solids	30- 70 ppm
Oil	50-110 ppm
Ammonia	20- 50 ppm
Phenols	3- 11 ppm
Sulfides	< 1- 2 ppm
Total Chromium	<0.1-0.4 ppm

It must be emphasized that the above concentrations refer to the wastewaters prior to any treatment or removal other than the primary removal of oil and suspended solids in an API or CPI oil-water separation unit.

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TABLE 7. REFINERY POLLUTANT LOADS AND THE EQUIVALENT WASTEWATER POLLUTANT CONCENTRATIONS

POLLUTANT LOAD as pounds of pollutant per thousand barrels of crude oil processed in refinery	*REFINERY CATEGORY*				
	TOPPING	*CRACKING*	*PETROCHEMICAL*	*LUBE OIL*	*INTEGRATED*
BOD_5	1.2	25.5	60.0	76.0	69.0
COD	13.0	76.0	162.0	190.0	115.0
TOC	2.8	14.5	52.0	38.0	48.6
Suspended solids	4.1	6.4	17.0	25.0	20.3
Oil	2.9	10.9	18.5	42.0	26.2
Ammonia	0.42	9.9	12.0	8.5	7.2
Phenols	0.012	1.4	2.7	2.9	1.3
Sulfides	0.019	0.33	0.30	0.005	0.70
Total chromium	0.0025	0.088	0.085	0.016	0.17
EQUIVALENT WASTEWATER POLLUTANT CONCENTRATION as ppm by weight in the wastewater flow					
BOD_5	7	122	240	203	173
COD	78	365	648	507	288
TOC	17	70	208	101	122
Suspended solids	25	31	68	67	51
Oil	17	52	74	112	66
Ammonia	3	48	48	23	18
Phenols	< 1	7	11	8	3
Sulfides	< 1	2	1	< 1	2
Total chromium	< 0.1	0.4	0.3	< 0.1	0.4

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FUTURE TRENDS

General

The future trends in petroleum refinery wastewater generation and the pollutants in wastewaters is a function of many inter-related variables. Perhaps the key variables affecting those future trends are those associated with:

- Future environmental regulations
- New refinery technology
- New refinery feedstocks
- Water reuse and conservation

Each of the above key variables are discussed in qualitative terms in this section. It would be very difficult if not impossible to quantify the future trends, and any attempt to do so is beyond the scope of this section.

FUTURE ENVIRONMENTAL REGULATIONS

The generation of wastewaters in refineries will be strongly influenced by the need to comply with the ever-increasing stringency of environmental regulations. This applies not only to effluent wastewater regulations. It applies just as well to regulations which are directed at air emissions and at solid wastes. The additional technology and facilities needed to comply with air emission and solid waste regulations very often results in additional water usage and additional wastewater generation. For example, if flue gas scrubbers are required on refinery boilers, process heaters and fluid catalytic cracking unit regenerators in order to meet future limitations on sulfur dioxide emissions, wastewater slurries may be generated which will require handling, treatment and disposal of a type not currently practiced in refineries.

As another example, future environmental regulations on the quality of refinery products such as on the permissible constituents of gasoline (for example, constraints on the aromatic content or tetraethyl lead content of gasolines) will have a direct effect on forcing changes in refinery processing or the development of new processes. Those changes or new technology will undoubtedly have an effect upon the generation and composition of refinery wastewaters.

Any future environmental regulations directed toward "toxic" or "hazardous" pollutant discharges will have a direct effect upon the wastewater treatment technology required at the "end of the pipe". However, such regulations may also require process changes or new processes to control the generation of such pollutants. Again, those changes or new processes may well have a secondary effect upon the generation of wastewaters.

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Obviously, any regulations directed toward an ultimate "zero discharge" goal would have a profound effect upon the generation of refinery wastewaters by forcing new technology for the reuse of treated wastewaters.

NEW REFINERY TECHNOLOGY

The development of new technology for petroleum refining is an on-going, evolutionary process. As the world's supply of petroleum crude oil diminishes and the "energy shortage" grows more and more severe, the search for new technology to obtain more gasoline and other products from each barrel of crude oil will be greatly intensified. The new technology that will emergy from that search will bring with it either additional problems or new problems related to wastewater generation.

While it is difficult to foresee just what new refinery technology is over the horizon, one can predict with some certainty that refineries will become increasingly complex. And it can be predicted that the increasing complexity will mean additional problems of wastewater generation and treatment. A brief comparison of the topping refinery and the integrated refinery categories in Tables 6 and 7 makes it obvious that increasing the complexity of refineries not only results in an increased wastewater generation but it also results in a higher level of pollutants within the wastewaters.

NEW REFINERY FEEDSTOCKS

As the world's supply of low-sulfur crude oil becomes scarcer, refineries will have to process increasingly higher-sulfur crude oils. As discussed earlier herein, processing higher-sulfur crude oils will require more and more hydrogen synthesis units in refineries. Since hydrogen synthesis has a very large steam demand, there will be an increase in the wastewaters generated by boiler feedwater treatment (softening or demineralization) and there will be an increase in the generation of high TDS boiler blowdown. Hydrogen synthesis also produces a process steam condensate which, if not reused as boiler feedwater, constitutes a major wastewater source.

The search for new or alternative energy supplies will inevitably lead to coal liquefaction and to extraction of oil from U.S. western shale deposits[7]. The crude oils from those sources will still require refining to produce the conventional range of petroleum refinery products. Those feedstocks will have very much higher nitrogen contents and sulfur contents than the low-sulfur crude oils currently processed in refineries. The processing of those new feedstocks will compound the need for additional hydrogen synthesis as well as possibly create new wastewater generation problems other than those associated with additional hydrogen synthesis.

WATER REUSE AND CONSERVATION

There is a vast body of technical literature regarding industrial wastewater reuse and conservation of fresh water intake. It is not the intent of this section to discuss the many reuse technologies that have been proposed. Nor is it the intent to review the

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histories of those specific cases in which water reuse has been successfully demonstrated or commercially practiced. However, it is quite safe to predict that there will be an increasing trend toward water reuse in industrial plants of all kinds in order to comply with environmental regulations.

As for petroleum refineries, their oily wastewaters can be treated so as to produce an effluent amenable to selected reuse within the refineries. However, most refineries have four wastewaters which contain a high level of inorganic salts (see Figure 8) and it will be most difficult to treat those four wastewaters for reuse:

- Desalter effluent brine
- Cooling tower blowdown
- Boiler blowdown
- Intake water treatment wastes (brines).

The technologies do in fact exist for desalination of such wastewaters, but they are very expensive and require a very large consumption of energy. Removal of the inorganic, water-soluble salts from those wastewaters creates the problem of how to dispose of the salts in a manner which prevents their dissolution in the next rainfall. In other words, desalination of wastewater brines and transport of the removed salt to a disposal dump merely transfers the problem without providing an ultimate resolution of the problem.

The trend towards water reuse and fresh water conservation in petroleum refineries will probably include:

- Replacement of once-through cooling water systems with circulating systems using evaporative cooling towers.
- Raising the level of concentration cycles within existing circulating cooling water systems by reducing the amount of blowdown.
- More usage of air-cooling rather than water-cooling.
- More intensive efforts to reduce water-cooling and steam-heating needs by utilizing more process heat recovery.
- Replacement of injected steam into refinery side-cut strippers by external, steam-heated reboilers in order to reduce the generation of sour condensates.
- Reuse of biotreated wastewaters (containing low levels of inorganic salts) in selected services such as low pressure boiler feedwater.
- More research into the problems of desalination and disposal of the resultant inorganic salt wastes.

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SECTION 4

A REVIEW OF POLLUTANTS IN PETROLEUM REFINERY WASTEWATERS AND EFFECTS ON AQUATIC ORGANISMS

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ORGANIC CHEMICALS

Petroleum refineries use water to wash the crude oil stock or fractions derived from the crude oil stock. The process of washing crude oil with water for removal of inorganic salts is referred to as desalting. During the desalting process, the contact water is contaminated with dissolved or emulsified organic chemicals from the crude oil stock. Water is also used for stripping of undesirable chemicals such as hydrogen sulfide and ammonia from overhead flue gases in thermal and thermo-catlytic process units. Condensed water from stripper units will also be contaminated with volatile organic chemicals produced by cracking of heavier hydrocarbons. Phenolic type compounds may occur at high concentration levels in stripper condensate waters. Several other compounds, such as chemical compounds used within the refinery to control scale and corrosion on cooling towers, to reduce frothing in desalters, and other miscellaneous uses, in addition to those originally present in the crude oil may be picked up as contaminants in the wastewater. Therefore, the potential number of organic chemical compounds which can occur in wastewater from a petroleum refinery is essentially equal to not only the number of compounds present in the original crude oil stock but also to that resulting from fracturing processes and chemical additives used within the refining operations.

It is beyond the scope of this section to discuss all of the organic chemical compounds which could potentially occur in petroleum refinery wastewaters. Essentially, any or all of the compounds identified in crude oils could occur at trace levels in either suspension, emulsion, or solution form in the wastewater. Several analyses of crude oils from various geographic locations and geological strata have indicated that while most crude oils contain many compounds in common, the percentage composition of these common compounds varies tremendously. Also, there may be uniquely different compounds in oils derived from different geological formations. The reader is referred to other reviews for a more detailed discussion of the organic chemical composition of crude oil[19,150].

The complexity of organic contaminants in petroleum refinery wastewaters has stimulated investigation and development of many different methods of extraction for isolation and identification of some or all of the components. For the sake of brevity, most of the isolation techniques can be grouped into major categories. A brief discussion of the techniques is presented.

Liquid/Liquid Extraction

This extraction procedure is based upon the principal of differential solubility of organic chemicals in polar and nonpolar solvents[153]. Water is a very polar solvent and, in relative terms, will not dissolve large quantities of nonpolar solutes such as hydrocarbon molecules. In contrast, nonpolar solvents such as hexane, benzene, and methylene chloride will, in relative terms, dissolve large quantities of nonpolar solutes. Mixing of two immiscible solvent phases such as water and hexane will result in a selective partitioning of the nonpolar solutes from the aqueous polar phase into the nonpolar hexane phase. If this process is repeated several times, most of the nonpolar solutes can be extracted from the aqueous polar phase into the nonpolar solvent phase. This procedure is widely used for extraction of nonpolar organic contaminants from water and wastewaters. The most extensive use of this procedure has been for extraction of pesticides and herbicides from water. Percentage recoveries of spiked samples have been 90 percent or better for most pesticides.

Adjustment of pH of the aqueous phase prior to extraction results in a change of the polarity of solutes in the aqueous phase. Organic acids exist as ionized polar molecules at neutral or alkaline pH's. A decrease in pH towards the acidic range will shift equilibria of the organic acids towards the un-ionized nonpolar form, which is more soluble in a nonpolar organic solvent. Similarly, adjustment of pH of an aqueous solution towards the alkaline range will shift ionization equilibria of basic organic molecules toward the un-ionized nonpolar form, which can then be extracted by a nonpolar organic solvent. By extraction of an aqueous solution with a nonpolar organic solvent at neutral, acidic, and alkaline pH's, three different groups of organic solutes can be isolated. This procedure simplifies the resultant extracted fractions and benefits subsequent identification. This procedure has been adopted by EPA for analysis of the "consent decree" priority pollutants. The protocol procedure calls for extraction of the water sample with pH adjusted to 12 to obtain a base-neutral fraction and subsequent extraction of the water with pH adjusted to 2 to obtain an acidic fraction.

Adsorption/Solvent Extraction

This procedure utilizes the unique property of some solid substances to adsorb nonpolar solutes from aqueous solutions. The most commonly used substance for this purpose is activated carbon. Activated carbon will adsorb approximately 20 to 30 percent of its weight of nonpolar organic solutes from an aqueous solution. This unique property has stimulated its use for concentrating trace organic chemicals from aqueous solutions[23]. The adsorbed compounds were sequentially extracted with a nonpolar organic solvent (chloroform) and a semi-polar organic solvent (ethanol) to obtain

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nonpolar and polar fraction, respectively. The carbon adsorption method (CAM) was successfully used to isolate and identify several organic compounds responsible for taste and odor problems in drinking water[23]. There have been numerous studies of the advantages and disadvantages of this procedure which have been reviewed[21,63].

Weber and Morris[180] reported that the rate-limiting factor in the carbon adsorption process was intraparticulate diffusion of the solute molecules within the micropore structure of the granular activated carbon. Aqueous solubility of the solute compound affects the initial surface adsorption. A slightly soluble organic compound with a structurally large molecule adsorbs rapidly from aqueous solution but diffuses slowly within the micropore structure of the carbon. Thus, the compound rapidly saturates the carbon surface and the adsorption rate declines rapidly. Thus the efficiency of activated carbon for extracting trace organic solutes from water appears to be related to two factors; i.e., surface adsorption and intraparticulate diffusion within the microporous structure of the activated carbon.

One of the major advantages of the CAM was the capability to adsorb trace levels (ng/ℓ or μg/ℓ) of organic contaminants from large volumes of water. The resultant chloroform extracts would yield several grams of organic contaminants which could then be further fractionated by classical solubility separation procedures. Prior to the advent of sensitive analytical instrumentation it was necessary to obtain gram quantities of extract to provide enough sample for identification of individual compounds.

Some of the disadvantages of the CAM were: non-quantitative recovery of some organic solutes from the activated carbon, catalytic or microbial mediated changes in chemical structure on the carbon surface, preferential adsorption of some solutes, and selective displacement of solutes[14,83,21].

Another solid adsorbent which has been used for concentrating trace organics from water is XAD-2 resin. This resin which is a polymer of styrene-divinyl benzene is classified as having a low polarity adsorption surface. Its efficiency has been evaluated by Junk[89] and varied from 89 percent for phenols extracted from acidified water to 101 percent for organic acids extracted from acidified water. The range of compounds tested were alcohols, aldehydes, esters, acids, phenols, halogenated compounds, polynuclear aromatics, alkyl benzenes, nitrogen, and sulfur containing compounds, pesticides and herbicides. The general procedure involves passage of from 1 to 100 liters of water through 2 grams of XAD-2 resin contained in a glass column. The adsorbed solutes are subsequently eluted with 25 mℓ of diethyl ether, which is then dried and concentrated to 1 mℓ. The concentrated eluates are subsequently analyzed by gas chromatography (GC) or a combination GC-mass spectrometry (MS).

Physical Extraction Techniques

The mixture of organic substances extracted by liquid/liquid extraction techniques or adsorption/solvent elution techniques are often too complex for adequate resolution by conventional GC. As a result, several physical separation techniques

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have been developed to isolate simpler fractions. One of the earliest methods utilized was steam distillation to extract volatile compounds which were subsequently extracted and concentrated in organic solvents. The resultant extract contained a less complicated mixture of organic compounds which could be resolved by conventional GC. Steam distillations have been used by Ogata and Miyake and Ogata and Ogura[132] to identify petroleum derived compounds causing odors in fish flesh, by Ackman and Noble[8] to identify petroleum hydrocarbons from tainted fish, by Dorris, et al.[53] to identify aliphatic hydrocarbons in oil refinery wastewaters.

Another procedure which has been developed recently is the use of an inert gas such as nitrogen or helium to strip volatile organic compounds from water which are adsorbed on a Tenax-GC trap. The compounds are subsequently thermally eluted directly onto a GC column for analysis[18]. This procedure has proven to be effective for analysis of volatile organic compounds in drinking water and industrial wastewaters. Several trihalomethanes, halogenated ethanes, and volatile hydrocarbons such as naphthalene, toluene, and benzene have been identified in surface waters using this technique[88].

ANALYTICAL INSTRUMENTATION

Gas Chromatography

A major obstacle to identification of trace organic contaminants has been the complexity of the mixture of organic compounds dissolved in wastewaters. Classical solubility separations are time consuming and usually not adequate for resolving complex mixtures into individual components for identification. Also, fractional distillations cannot resolve individual compounds from complex mixtures. In gas liquid chromatography (GLC), the separation of a mixture of organic compounds is dependent upon partitioning between a moving gaseous phase and a stationary liquid phase coated on an inert support. Differences in affinity of the individual compounds for liquid phase results in a varying partition rate between the moving gas phase and the stationary phase and therefore separation ensues[91,75]. In GLC, separation or resolution of compounds depends upon the equilibrium distribution of substances between the gas phase and the column stationary liquid phase. For fixed conditions of gas flow, column material, size and length, temperature, etc., there is a specific elution time for most chemical constituents. Therefore the chromatographic column is the heart of any GC instrument, and the degree of resolution that can be obtained is dependent upon the characteristics of the column.

Perhaps the best example of the value of GC for separation and identification of complex mixtures of organic compounds was the progress made on the API Project #6. In 1927, API established research project #6 at the National Bureau of Standards. In 1950, the project was moved to the Carnegie Mellon Institute of Technology in Pittsburgh, Pennsylvania. In the early years of this investigation, only systematic distillation was used until around 1935 when fractionation by selective adsorption on silica or alumina was also introduced. It was not until 1956, when GLC finally came into use for separations. Rossini reported isolation of 175 hydrocarbon compounds from the crude oil. This was the result of 33 man-years of work. In 1961, Desty reported on the GC analysis

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of the C_4 through C_9 fraction of Ponca crude, representing about 30 weight percent of the total crude oil. By using a 900 feet x 0.006 inch ID glass open tubular column having over 1 million effective plates and operated at room temperature, 122 peaks were resolved in 24 hours. In contrast, in the API project #6 only 89 hydrocarbons had been separated in this region.

Capillary columns have long been recognized as probably the types of columns which had the greatest potential for resolution of the complex mixtures of organic compounds extracted from water. However, capillary columns can accommodate only very small injection volumes without overloading and subsequent loss of resolution. The maximum quantity of sample which could be injected ranged from 0.01 to 0.1 μℓ including the carrier solvent. This limitation lead to the development of special attachments which split the injection 100:1 or 1000:1, venting most of the sample away from the column. Most environmental contaminants can occur at concentrations of a few ng/ℓ or μg/ℓ and GC detectors could not detect the small quantities of compounds after split injection. This limitation prevented successful application of capillary column GC for analysis of environmental contaminants. Therefore most of the analyses have been performed with packed columns which could be injected with from 1 to 10 μℓ of sample without affecting resolution of the mixture, but had limited resolution for very complex mixtures. However several researchers successfully used GLC retention times on packed columns to identify trace organic compounds extracted from surface waters[14,38,79].

The GC was combined with other confirmatory techniques such as infrared to identify compounds associated with petroleum refinery wastes[148] and MS to identify petroleum products[118]. These investigations were perhaps influential in the development of combined GC with MS, the most powerful analytical development at the present time.

Combination Gas Chromatograph-Mass Spectrometer System

Two developments have occurred within the last few years which have significantly improved capabilities to identify trace organic contaminants in water and wastewaters. Perhaps the most significant was development of a combined GC-MS system. Early attempts to combine the GC with the MS encountered many problems. One of the most troublesome was the interface between the two instruments. The GC uses high pressure carrier gas as the mobile phase to affect separation of the compounds, whereas the analyzer section of an MS must maintain a high vacuum of approximately 10^{-4} Torr. Therefore, special interfaces had to be developed which could remove most of the carrier gas without removing all of the organic compounds of interest. A second major problem was the time of elution of a chromatographic peak. Many peaks from GC columns elute within seconds or at least fractions of a minute. Existing MS usually require several minutes to scan a compound. Therefore an MS which could scan a GC peak in a few seconds or less had to be developed.

Another major development was the splitless injection technique of Grob and Grob[71]. This technique permitted injection of samples dissolved in a solvent without splitting, which prevents loss of sensitivity without overloading the capillary column with

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solvent. With the aid of the Grob-type splitless injection technique, glass capillary GC with up to 600,000 theoretical plates can be used to resolve up to 125-150 specific compounds. Combining the resolution capability of glass capillary GC to separate complex mixtures with the capability of the MS to provide molecular weight and election impact fragmentation data has resulted in the most powerful instrument ever developed for analysis of environmental contaminants. A simultaneous development of computers capable of rapidly accumulating the data from the MS was also necessary to permit full utilization of the capability of the combination GC-MS.

The impact of these developments is clearly illustrated by the fact that in 1970 only 66 specific organic chemical compounds had been positively identified in surface freshwaters of the world. In 1975, Junk reported identification of over 300 specific organic compounds from drinking water alone. In a recent symposium on "Identification and Analysis of Organic Pollutants in Water," 31 of 36 papers used GC-MS as the major instrumental technique[92].

Another factor which has had a major impact upon the current state of knowledge concerning the composition of trace organic compounds in wastewaters was the consent decree established between the Natural Resources Defense Council and the Director of EPA, Russell Train. This decree mandated EPA to perform a survey of 128 priority pollutants in industrial wastewaters to determine if these toxic or deleterious compounds were being discharged in final effluents. This judicial decree initiated the most intensive and broad-scale investigation of trace organic contaminants in the world. The API collaborated with EPA in a survey of 17 oil refineries to determine if any of the 128 priority pollutants were present in either the influent feedwater, the influent wastewater, the influent wastewater to the treatment system, or persisting after treatment in the final effluent[10].

COMPOUNDS IDENTIFIED IN OIL REFINERY WASTEWATERS

Prior to development of combination GC-MS, most investigators were unsuccessful at identification of specific organic contaminants in oil refinery wastewaters. Researchers in the 1950 to 1970 period used GC retention times as one of the major analytical parameters. Solvent extracts from oil refinery wastewaters were so complex, that the chromatograms contained many unresolved peaks. A large number of unresolved peaks were often encountered in the region between where n-decane and dodecane standard hydrocarbons would elute. The unresolved peaks were so numerous that the chromatograph contained a hump in this region. This was encountered so frequently, that it was used as a distinguishing characteristic for petroleum derived chemical contaminants.

Rosen and Middleton[148] used the carbon adsorption method to concentrate trace organic compounds from lake water in order to obtain sufficient quantities of organic compounds to identify. The compounds were solvent extracted from the activated carbon and chromatographed on silica gel columns to obtain aliphatic, aromatic, and oxygenated groups of compounds. The resultant fractions were analyzed by infrared (IR) spectrophotometry. The IR "fingerprint" spectra of extracts from the lake water were similar to

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extracts from an oil refinery wastewater. Thus, although specific compounds could not be identified, similarities of the IR spectra were judged sufficient to indicate contamination of the lake water by aliphatic and aromatic compounds discharged from the refinery.

A similar procedure was used by Middleton, et al.[122] to isolate odoriferous compounds from the drinking water supply of Nitro, West Virginia. The steam volatile aromatic fraction was the most odorific. The IR spectra of this fraction was very similar to that of kerosine (APCO blend).

Melpolder, et al.[118] demonstrated the utility of MS to identify and quantify known mixtures of petroleum type hydrocarbons in aqueous solutions. The hydrocarbons were stripped from the aqueous solutions with hydrogen gas and collected on liquid nitrogen traps. The collected compounds were thermally eluted into an MS through a sintered glass inlet. Quantitative recoveries were obtained for levels of kerosine and furnace oil at 0.1 mg/ℓ, gasoline at 0.01 mg/ℓ, and a standard mixture of hydrocarbons from pentane (C_5H_{12}) to decane ($C_{10}H_{22}$) at 0.014 mg/ℓ.

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In 1967, Brady presented a summary of an API sponsored project conducted by A. D. Little, Inc., to identify the taste and odor causing compounds in oil refinery wastewaters. Using pentane extraction, column chromatography, GC, and high resolution MS; the investigators were able to identify several groups of compounds in odor-rich fractions. A group of compounds responsible for the "burnt-rubber" odor was identified as diaryl sulfides. One particularly odorific compound identified in this group was diphenyl disulfide. Other compounds identified in this fraction were dimethyl naphthalene and dimethyl anthracene.

Steam distillation fractions of oil refinery wastewaters appeared to concentrate acutely lethal substances from oil refinery wastewaters as indicated by acute static *Daphnia* bioassays[53]. Solvent extracts of the steam volatile fraction were subjected to analysis by GC-MS. A homologous series of normal aliphatic hydrocarbons from n-undecane ($C_{11}H_{24}$) to n-octadecane ($C_{18}H_{38}$) was identified in extracts from four different refineries. The compounds m-cresol and dioctyl phthalate were identified in extracts from two different refineries, however no compounds were identified which could fully account for the acutely lethal effects observed.

Burlingame, et al.[33] analyzed solvent extracts from three different locations at an oil refinery wastewater treatment plant. The extracts were designated as phenolic, acidic, basic, and neutral fractions based upon pH of wastewater during extraction. The extracts were analyzed on a capillary column GC-high resolution MS with computer analysis of the data. Based upon the mass spectral data, four specific compounds in the phenolic fraction and one in the acidic fraction were identified (Table 8). In addition, 11 different classes of compounds were detected in the acidic fraction and 15 different classes of compounds in the neutral fraction (Table 9). There were several isomers present within most classes of compounds. Most of the compounds or classes of compounds identified by Burlingame, et al.[33] have been identified as components of crude oils by

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TABLE 8. PARTIAL LIST OF COMPOUNDS IDENTIFIED IN EXTRACTS FROM OIL REFINERY WASTEWATERS (MODIFIED FROM BURLINGAME, ET AL., 1976)

Compound Type	Formula	Present in No. of Scans	Fraction Phenolic	Acidic
Anisole	C_7H_8O	1	×	×
Methyl Anisole	$C_8H_{10}O$	1	×	
C_2 Anisole	$C_9H_{12}O$	1	×	
Methyl Benzoate	$C_8H_8O_2$	1	×	×
Saturated Methyl esters	$C_nH_{2n}O_2$	28		×
Saturated Ethyl esters	$C_nH_{2n}O_2$	6		×
Olefinic Ethyl esters	$C_nH_{2n-2}O_2$	1		×
Saturated Propyl esters	$C_nH_{2n}O_2$	1		×
Cyclic Alkyl Methyl esters	$C_nH_{2n-2}O_2$	4		×
Alkyl-sub. Methyl Benzoates	$C_nH_{2n-8}O_2$	16		×
Phenylalkyl Methyl esters	$C_nH_{2n-8}O_2$	5		×
Alkyl-sub. Naphthenic Methyl esters	$C_nH_{2n-8}O_2$	8		×
Indenic Methyl esters	$C_nH_{2n-12}O_2$	1		×
Sulfur-sub. Aromatic Methyl esters	$C_nH_{2n-6}O_2S$	3		×
Alkyl-sub. Methyl sulfides	$C_nH_{2n-6}S$	1		×

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TABLE 9. PARTIAL LIST OF COMPOUNDS IDENTIFIED IN NEUTRAL EXTRACTS FROM OIL REFINERY WASTEWATERS BY BURLINGAME, ET AL., 1976

Compound Type	Formula	Sample location		
		K-1-N	K-2-N	K-3-N
n-alkanes	C_nH_{2n+2}	n = 11-33	n = 12-33	n = 15
branched alkanes	C_nH_{2n+2}	series		n. d.
mono-saturated or mono-cyclic alkanes	C_nH_{2n}	n = 11-28	n. d.	n. d.
alkyl benzenes	C_nH_{2n-6}	n = 9 (3) n = 10 (6) *n = 11	n = 9 n = 10 (yes)	n = 8 (2) n = 9 (3) n = 10 (3)
naphthalenes	C_nH_{2n-12}	*n = 10-13 (several)	n = 10-14	n = 12-14 (yes)
phenanthrenes or anthracenes	C_nH_{2n-18}	n = 14-19	n = 14-19 **n = 17	n = 15-17 trace
pyrene or fluoroanthrene	C_nH_{2n-22}	n = 16 minor	n = 16 minor	n. d.
alkyl biphenyls	C_nH_{2n-14}	n = 13 significant n = 14	n. d.	n = 12 n = 13 trace
methyl indan	$C_{10}H_{12}$	trace	n. d.	n. d.
alkylated phenols	$C_nH_{2n-6}O$	n = 7-12 *n = 8 & 9		n = 7-13
Thiacyclanes	$C_nH_{2n}S$	n = 6 n = 8	n = 8-11	n = 6-11 (several)
benzothiophenes	$C_nH_{2n-10}S$	n = 8-12	n = 8-11	n = 9 n = 10 (few)

* major constituent of extract.

** relatively abundant

Numbers in parentheses indicate number of isomers detected.

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previous researchers. Therefore, Burlingame's analyses confirm what many researchers have suspected; any compound originally present in crude oil could potentially occur in oil refinery wastewaters. Perhaps the most significant result of their analyses was the detection of some isomers of n-alkanes, alkyl benzenes, naphthalenes, phenanthrenes or anthracenes, alkyl biphenyls, etc. in the influent and effluent from the biological treatment system. These results confirm that some classes of compounds are resistant to biological treatment and may persist in the final effluents.

Raphaelian and Harrison[144] analyzed 24-hour composite samples of wastewaters from dissolved air flotation (DAF) and final clarifier (FC) units of Class B refinery activated sludge treatment system. Solvent extracted neutral, acidic, and basic fractions from the wastewater were analyzed by Grob-type splitless injection glass capillary GC-MS. Over 300 compounds were identified in the neutral fraction from the DAF unit wastewaters based upon GC retention time and presence of major ions in mass spectral scans. The concentration of the compounds was semi-quantified by either the area or peak height of major ions in the mass spectra (Table 10). In addition, Raphaelian and Harrison also analyzed the trace organics after passage of the oil refinery wastewater through a mixed-media filter/activated carbon (MMF/AC) pilot-scale treatment system. Identification of over 300 compounds in the neutral fraction from the DAF unit wastewaters illustrates the complexity of organic contamination in oil refinery effluents. The majority of the compounds identified were aromatic and alkylaromatic types.

The relative efficiency of biological and MMF/AC treatment systems for removal of specific compounds can be determined from Raphaelian and Harrison's data. The activated sludge unit was more effective in removal of aromatic than long chain aliphatic hydrocarbons. The long chain aliphatic hydrocarbons, greater than C_{10}, were especially difficult to remove. The effectiveness of the activated sludge treatment system for removal of polynuclear aromatics could not be determined since the concentrations of these compounds were too low for accurate quantification.

Several organic compounds were detected in final effluents during the cooperative survey of 17 petroleum refineries by the EPA and API. The most frequently detected compounds were methylene chloride, benzene, toluene, chloroform, trichloroethylene, ethyl benzene, pyrene, di-n-butyl phthalate, and bis(2-ethylhexyl) phthalate. The concentrations of these contaminants ranged from less than detectable to a maximum of 60 μg/ℓ.

A significant result of the cooperative EPA-API survey was a measure of the accuracy and reproducibility of analyses for trace organics. The range in percent recovery of spiked samples for polynuclear aromatics was from 56 to 72 percent for the 5 to 20 μg/ℓ range and from 78 to 104 percent for the 33 to 220 μg/ℓ range. The overall percent recovery of phenol spikes was 65 percent and the quantity of the spike did not appear to affect extraction efficiency. The efficiency of liquid/liquid extraction for recovery of phthalate spikes was very erratic with a range from 4 to 300 percent. Overall, the accuracy and reproducibility of the liquid/liquid extraction procedure appears to be inadequate at this time. Considerable effort should be expended to improve the

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TABLE 10. LIST OF ORGANIC COMPOUNDS IDENTIFIED OR DETECTED IN NEUTRAL EXTRACTS FROM THE EFFLUENTS FROM A DISSOLVED AIR FLOTATION (DAF), AN ACTIVATED SLUDGE FINAL CLARIFIER (FC), OR A PILOT-SCALE MIXED-MEDIA FILTER/ACTIVATED CARBON (MMF/AC) TREATMENT SYSTEM, MODIFIED FROM RAPHAELIAN AND HARRISON, 1978

Compound Name	Relative Conc. in DAF Neutral Fraction	Presence(+), Absence(-) (FC effluent)	Presence(+), Absence(-) (MMF/AC effluent)
Chloroform	high	+	+
1,1,1-trichloroethane	high	+	+
benzene	medium	+	+
carbon tetrachloride	high	+	+
cyclohexene	high	+	+
toluene	high	+	+
ethyl benzene	low	+	+
p-xylene	high	+	+
m-xylene	high	+	+
o-xylene	medium	+	+
n-nonane	low	+	-
i-propyl benzene	trace	+	-
n-propyl benzene	low	+	-
m-ethyl toluene	medium	+	-
p-ethyl toluene	medium	+	-
1,3,5-trimethyl benzene	low	+	-
o-ethyl toluene	low	+	T
1,2,4-trimethyl benzene	high	+	+
cycloalkane	trace/medium	T/+	-
i-butyl benzene	trace	+	-
s-butyl benzene	trace	+	-
n-decane	medium	+	-
1,2,3-trimethyl benzene	medium	+	+
m-isopropyl toluene	trace	T	-
o-isopropyl toluene	trace	-	-
p-isopropyl toluene	trace	-	-
indan	medium	+	+
indene	trace	+	-
m-diethyl benzene	low	T	-
m-n-propyl toluene	low	+	-
p-n-propyl toluene	low	+	-
n-butyl benzene	trace	T	-
1,3-dimethyl-5-ethyl benzene	low	+	-
o-n-propyl toluene	low	+	-
1,4-dimethyl-2-ethyl benzene	low	NM	NM
ethyl styrene	low	-	-
1,3-dimethyl-4-ethyl benzene	low	+	-
ethyl styrene	medium	+	-
1,2-dimethyl-4-ethyl benzene	low	+	-

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TABLE 10 continued

Compound Name	Relative Conc. in DAF Neutral Fraction	Presence(+), Absence(-) (FC effluent)	Presence(+), Absence(-) (MMF/AC effluent)
1,3-dimethyl-2-ethyl benzene	low	-	-
1,2-dimethyl-3-ethyl benzene	low	T	-
C_5-benzene	trace	NM	NM
1,2,4,5-tetramethyl benzene	low	+	-
1,2,3,5-tetramethyl benzene	medium	+	+
n-undecane	high	+	-
2-methyl indan	medium	T	-
1-methyl indan	medium	+	-
1,2,3,4-tetramethyl benzene	medium	+	-
tetralin	low	-	-
naphthalene	high	+	+
C_6-benzene (16)	trace	+	-
n-dodecane	high	+	+
ethyl indan	low	-	-
C_{13}-alkane	high	+	-
dimethyl indan (3)	medium	T	T
methyl tetralin	medium	T	-
C_3-indan	trace	-	-
methyl benzothiophene (4)	low	+	-
methyl ethyl indan	trace	-	-
2-methyl naphthalene	high	+	+
trimethyl indan (3)	trace	-	-
C_4-indan/C_3-tetralin (7)	trace	+/-	-
dimethyl tetralin	low	T	-
n-tridecane	high	+	+
biphenyl	low	+	T
dimethyl benzothiophene (5)	trace	+	-
ethyl benzothiophene (2)	trace	+	-
ethyl naphthalene	medium	+	
dimethyl naphthalene (6)	high	+	+
C_{14}-alkane (2)	high	+	+
n-tetradecane	high	+	+
acenaphthene	trace	+	-
methyl biphenyl (2)	low	+	-
C_3-naphthalene (14)	low to high	+	+
C_{15}-alkane	high	+	+
n-pentadecane	high	+	+
fluorene	low	NM	NM
C_2-biphenyl (4)	trace	NM	-
methyl acenaphthene (3)	low	NM/+	-
n-hexadecane	high	+	+

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TABLE 10 continued

Compound Name	Relative Conc. in DAF Neutral Fraction	Presence(+), Absence(-) (FC effluent)	Presence(+), Absence(-) (MMF/AC effluent
C_3-biphenyl (5)	trace	NM	-
methyl fluorene (3)	low	+	-/T
C_2-acenaphthene (5)	low	NM	-
n-heptadecane	high	+	+
dibenzothiophene	low	T	-
pristane	high	+	-
anthracene/phenanthrene	high	+	+
C_2-fluorene (7)	low	NM	-
n-octadecane	high	+	+
methyl dibensothiophene (2)	low	NM/+	-
phytane	medium	+	+
methyl phenanthrene (3)	medium	NM	T
2-methyl anthracene	low	+	T
1-methyl anthracene	low	+	T
C_3 fluorene (2)	trace	+	T/-
n-nonadecane	high	+	+
C_2-dibenzothiophene	trace	-	-
C_2-phenanthrene/anthracene (8)	trace/low	-/+	-
fluoranthrene	trace	NM	-
C_2-phenanthracene/anthracene	trace	NM	-
n-eicosane	high	+	+
C_3-phenanthrene/anthracene (6)	trace	NM/T	-
pyrene	low	+	-
n-heneicosane	medium	+	+
$C_{17}H_{12}$ PNA (6)	trace	NM/T	-
n-docosane	medium	+	+
$C_{18}H_{14}$ PNA (3)	trace	+/T	-
chrysene	trace	+	-
1,2-benzanthracene	low	+	-
n-tetracosane	low	+	+
n-pentacosane	low	+	NM
phthalate (2)	medium/high	+	+

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accuracy and precision of this procedure or to develop new and better procedures.

The results cited in this review illustrate the rapid advances in analyses of trace organics which have occurred since the development of commercial computerized GC-MS systems. Additional investigations in the next few years will undoubtedly identify many more new organic compounds. Detailed knowledge of chemical compounds in the influent and effluent streams from wastewater treatment systems will permit more realistic evaluations of their effectiveness. In addition, delerterious effects of oil refinery wastewaters upon aquatic organisms can be correlated with concentration of specific toxicants rather than attempting to correlate with collective measures of organic chemicals such as COD or BOD.

EFFECTS OF PETROLEUM REFINERY WASTEWATERS

Acute Lethal Effects

Short term lethal effects of wastewaters are customarily determined with a bioassay test. Basically, this test consists of exposing a number of individuals (6-10) of the same species of organism to selected percentage concentrations of a wastewater for a predetermined interval of time (1-4 days) and recording response of the organisms. Death of test organisms, sometimes referred to as the quantal or "all or none" response, is an easily recognized and the most frequently used measure of effect. The most reproducible measure of response of a group of organisms is the median or 50 percent response. Therefore, the results of acute tests are usually expressed as median lethal concentration or median tolerance level for a specified time of exposure, i.e., 96 hour LC50 or 96 hour TL_m. The specific procedures for performance of acute toxicity tests with aquatic organisms are presented in detail elsewhere (Doudoroff, et al., APHA, and EPA). Therefore, a detailed discussion will not be presented in this section. However, some of the subjective decisions which may affect the results of the test and possibly the interpretation of the data will be discussed.

The choice of dilution water is very important because of the probable occurrence of other chemicals in the dilution water which could affect the toxicity of some contaminants in the effluent. If possible, dilution water should be obtained from the receiving stream above the point of wastewater discharge. Change in pH can increase or decrease the lethal effects of ammonia (Wurhmann and Woker[186]), hydrogen sulfide (Smith, et al.), and cyanide (Doudoroff[57]). In general, shifts in pH which result in greater concentration of the un-ionized equilibrium form result in an increase in lethal effects of the contaminant. Increases in hardness of water decrease the lethal effects of heavy metals (Mount; Pickering and Henderson[138]) and also the presence of organic chelators decrease the lethal effects of heavy metals (Sprague, et al.[157]). Lee[99] presented a good summary of many chemical factors which should be considered in toxicity testing. Obviously, the dilution water should duplicate conditions in the receiving stream, after allowance for mixing, as near as possible. If water from the receiving stream cannot be used for dilution, then the following choices should be considered in order of preference; untreated well water, reconstituted water prepared from distilled

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water, and dechlorinated tap-water.

It is preferable to use continuous-flow for exposure of test organisms to wastewaters due to the potential for a decrease in dissolved oxygen concentration and an increase in metabolic waste products in static methods of exposure. A comparison of 96 hour LC50's of fathead minnows exposed to oil refinery wastewaters in continuous-flow versus static conditions indicated that the continuous-flow exposure was not as lethal as the static exposure (Kleinholz[93]). The differences in 96 hour LC50 were not statistically significant between the two methods of exposure, however the fish in the continuous-flow tests appeared healthier.

Species of aquatic organisms differ in susceptibility to chemical toxicants and therefore care must be used in selection of a species for testing. Within the fishes, salmonid species such as rainbow trout and salmon are considered to be more susceptible than most warm water fishes such as largemouth bass, sunfish, and channel catfish. Irwin[87] compared the susceptibility of 57 different species of fish by performing 96 hour static acute toxicity bioassays of an oil refinery wastewater. The response was used to rank the species of fish relative to the most resistant, the common guppy (*Lebestes reticulatus*), which was assigned a value of 100.00. The relative ranking of some fish commonly used in bioassay tests were: mosquito fish (*Gambusia affinis*), 74.02; channel catfish (*Ictalurus punctatus*), 60.15; goldfish (*Carassius auratus*), 51.95; fathead minnow (*Pimephales promelas*), 49.19; bluegill sunfish (*Lepomis macrochirus*), 54.10; and rainbow trout (*Salmo gairdneri*), 34.68. The aquatic invertebrate species have not been used extensively as test organisms, therefore it is difficult to make generalizations concerning their relative susceptibility to chemical toxicants. The water flea (*Daphnia* sp.) is the most commonly used and is much more sensitive than most species of fish[11].

Acute toxicity bioassay tests of oil refinery wastewaters with fish indicate that effluents from properly operated biological treatment systems do not cause greater than 50 percent mortality of fathead minnows or rainbow trout[136]. Properly operated secondary biological wastewater treatment systems can produce final effluents which cause no mortality in 96 hours at 100 percent (undiluted) concentrations. Matthews[113] found that activated sludge treatment systems reduced the toxicity of the influent feed water from 18-56 percent (volume/volume percent dilution) to 100 percent in the final effluent as measured by 24 hour TL_{50} in four different refineries.

The Oil Refiners Waste Control Council (ORWCC) in Oklahoma has been cooperating with Oklahoma State University (OSU) in a monthly acute toxicity testing program since 1959. These acute toxicity tests are performed in accordance with APHA standard methods for static 96 hour fish bioassay tests[55]. Graham and Dorris[70] reported some of the data generated by OSU-ORWCC for 1960-1962. The wastewaters from refineries which used either activated sludge or waste stabilization lagoons consistently had a mean annual TL_m of greater than 100 percent, i.e., more than 50 percent of the test fish could survive in 100 percent effluent. Wastewaters from refineries which had not been treated adequately with some type of biological secondary treatment system were extremely toxic, with a mean annual TL_m of 19 and 21, respectively.

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Since Graham and Dorris[70] reported their data, all of the refineries within the ORWCC have installed the equivalent of activated sludge secondary treatment or better. All final effluents tested in the last five years have consistently had TL_m's greater than 100 percent. In fact, the method of reporting data has been changed to the convention of reporting TL_{100}; i.e., the concentration (percentage of effluent) in which 100 percent of the test organisms will survive.

Graham and Dorris[70] also performed 32-day continuous-flow fathead minnow bioassays. Wastewaters which were highly toxic in 96 hour acute tests had to be diluted by 90 percent to obtain greater than 80 percent survival. Wastewaters from the biological treatment units were relatively non-toxic in short term tests; i.e., 23/25 or 92 percent of the dilutions tested had greater than 90 percent survival after 96-hour exposure. However, the wastewaters contained chemical toxicants which had either delayed or cumulative effects; i.e., 17/25 or 68 percent of the dilutions tested after 16 days of exposure had greater than 90 percent survival whereas only 9/25 or 36 percent had greater than 90 percent survival after 32 days of exposure. Graham and Dorris observed that many fish appeared to stop feeding and appeared emaciated prior to death. The observation was supported by the condition index, K = weight in grams times 100,000 divided by total length in mm^3 (Carlander), which was uniformly 0.52 for all fish that died, indicating that death occurred when the fish reached a certain degree of emaciation.

Coté[45] reviewed the literature on effects of oil refinery wastewaters upon aquatic organisms and was unable to locate many articles. Most of the articles were concerned with the effects of compounds identified from crude oil or crude oil spills. Coté also reported on the results of some acute toxicity rainbow trout bioassays performed on Canadian oil refinery effluents. In general, effluents which had been adequately treated in biological systems caused less than 50 percent mortality of rainbow trout at 100 percent concentration for 96 hour exposure. Pessah, et al.[136] reported similar results on Canadian petroleum refinery wastewaters.

In the most comprehensive study located, Sprague, et al.[163] performed several types of sublethal tests in order to determine: (1) the sublethal effects of biologically treated oil refinery effluents, and (2) the type of test which appeared to yield the best measure of sublethal effects in the shortest interval of time and was simple to perform. They used rainbow trout, small tropical flagfish, and Daphnia magna as test organisms in long term continuous-flow exposures to the wastewaters. Wastewaters were collected and transported to the laboratory for performing the tests. Most of the effluent samples tested over a two-year period were considered to be non-lethal based upon 96 hour rainblow trout bioassays. Growth of rainbow trout indicated a threshold level in the vicinity of 9.4 percent effluent. The threshold concentration in a 3.5-month chronic test of flagfish was about 9.1 percent for an appreciable effect on final size of males. However, major effects were only observed in 28 percent or higher concentration of effluent. A significant increase in cough-reflex response by rainbow trout occurred between 25 and 50 percent effluent. Daphnia experienced a 50 percent failure in reproduction when exposed to 3.1 percent of the effluent for 14 days. The "safe" level at which only 5 percent impairment of Daphnia reproduction would occur was predicted to be 0.52

percent effluent.

The fish cough-reflex has been suggested to be very promising for predicting potential long-term effects based upon responses obtained during short-term tests. Carlson and Drummond[37] used the fish cough-reflex of bluegill sunfish to measure the effects of an activated sludge treated oil refinery wastewater. Analyses of three different effluent samples collected over an 8-month period of time, showed the effluent caused significant increases in coughs at concentrations as low as 0.8 percent following an upset in the biological treatment system. After the system had returned to normal, 12 percent effluent caused a significant increase in cough frequency. Previous investigators had detected a 200 percent increase in rate of coughs at concentrations of zinc just above the LC_{50} value of 6.0 mg/ℓ. A large and rapid rise in frequency of cough-reflex of fish exposed to wastewaters or chemical toxicants indicates potential toxic effects. Smaller increases in frequency of cough responses may be indicative of potentially sublethal long-term effects. Sprague, et al.[163] detected the threshold of significant increase in frequency of coughs by rainbow trout at between 25-50 percent oil refinery wastewater. In contrast, the "safe" level of effluent for *Daphnia* was predicted to be 0.52 percent effluent.

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The detection of an increase in tumors in fish collected from a polluted river may have serious implications for long-term contamination with trace levels of chemical toxicants. Brown, et al.[24] found 4.48 percent of the fish collected from the polluted Fox River had tumorous growths compared to only 1.03 percent in fish from a non-polluted river. Several classes of contaminants were detected in the polluted river; crude oil, gasoline, aromatic hydrocarbons, polynuclear aromatics, ethers, organic acids, organophosphates, triazines, and chlorinated hydrocarbons. The concentrations ranged from 0.002 to 0.1 mg/ℓ. In subsequent articles, Brown, et al. also showed an increase in incidence of disease in fish from the polluted river compared to the fish from the non-polluted river. The increase in tumors in fish from the polluted river may have been partly due to an increase in viral infections[24].

The acute toxicity of oil refinery wastewaters has been demonstrated with many different types of tests. *Daphnia* sp. have frequently been used as very sensitive bioassay organisms for comparison of other tests[163]. Although *Daphnia* have long been recognized as a very sensitive bioassay organism, they have not been widely used because of unexplainable mortality in laboratory cultures and in controls. Buikema, et al. performed some inter-laboratory *Daphnia* sp. bioassay tests to determine reproducibility of the test. Their results indicated that refinery personnel could be quickly trained to obtain satisfactory reproducibility with *Daphnia* bioassays. Richardson, et al.[147] showed cell culture assays of oil refinery wastewaters to be more sensitive than 24-hour *Daphnia* bioassays. The cell culture assay would permit exposure of two generations of cells during a 40-hour test and thus could be valuable for detecting mutagenic effects in a short period of time. Another short-term test using enzyme inhibition studies of glucose-6-phosphate dehydrogenase was more sensitive than fish bioassays but not *Daphnia* or grass shrimp bioassays (Rutherford, et al.). The grass shrimp (*Palaemonetes pugio*) has been found to be as sensitive as *Daphnia* for detecting acute lethal effects of oil refinery wastewaters[72].

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The chemical toxicants in oil refinery wastewaters which cause short-term acute toxicity can be removed by good biological treatment systems. These substances have not been identified and probably will not be since most refineries within the U.S. have the equivalent of biological treatment or better. However, as some long-term toxicity tests have shown, biological treatment generally does not remove all chemical toxicants. Some substances persist which have been shown to be lethal after 16 to 32 days of exposure[70, 30]. These substances can be removed by activated carbon adsorption, which indicates that the substances may be organic in nature. Many of the acutely lethal components of oil refinery wastewaters can be removed by simple steam stripping, which would indicate volatile substances[53]. Since the long-term toxicity can be reduced by activated carbon treatment, it would indicate that these components are organic in nature. In the EPA-API survey of priority pollutants, most of the compounds identified in the base-neutral fraction would have to be judged deleterious to organisms in the receiving environments.

Long-Term Effects

The long-term effects of any chemical toxicant are difficult to measure and even more difficult to predict. The effects may be lethal to selected stages in the life cycle of the organism and might not be detected in short-term tests. Larval stages of fish and aquatic invertebrates seem to be especially susceptable. Chemical toxicants can also affect the ability of an organism to escape predators or pursue food and thus indirectly impair the organisms chance of survival. Other sublethal long-term effects may result in a change in the normal behavior pattern of organisms and thus impair spawning activities[177] or affect response time of avoidance reflexes[181]. Since the long-term effects of even single chemical toxicants are difficult to measure, there have been few investigations of the long-term effects of complex mixtures such as petroleum refinery wastewaters.

One method that has been used to obtain an integrated assessment of the effects of all environmental factors is an evaluation of the structure of the biological communities in receiving waters. The balance of aquatic communities can be used as integrated response to many different stresses such as chemical pollution, artificial enrichment, or severe changes in physical factors (Hawkes). Wilhm and Dorris[182] utilized this technique to assess the combined effects of municipal and oil refinery wastewater discharges into a creek. A numerical index, diversity of the distribution of individual organisms among species, was used to compare effects at various distances downstream from the discharges. The diversity index of the benthic macroinvertebrate organisms directly below the discharges was less than 1.0, whereas it was greater than 3.0 downstream a distance of 60 km. Wilhm and Dorris proposed that a species diversity index of less than 1.0 indicated a severe effect upon the benthic community, whereas diversity indices of greater than 3.0 indicated a non-disturbed community.

Although numerical indices have been criticized for over-simplification and for not being sensitive to rare species, several indices have proven to be very useful for summarizing large quantities of biological data. Several indices should be used to

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provide the maximum amount of information possible. In some cases, the disappearance of species of organisms known to be sensitive to chemical toxicants should be used to supplement the numerical indices.

The long-term effects of a bunker oil spill in a river was studied over a two-year period following the spill[116]. Many species of phytoplankton and benthic macroinvertebrates were eliminated after the spill. Using the indicator species approach, McCauley showed that *Gammarus*, *Agrion* nymphs, and *Dugesia* disappeared from the benthic community after the spill. The tolerant species of *Tubifex*, *Tendipes* larvae, *Nemata* and and *Hirudinea* remained in the area after the spill. Thus the presence or absence of sensitive species can sometimes be used to interpret water quality. However, this approach must be used with caution since many factors other than pollution can affect the desirability of the environment for a particular species.

Periphyton, a collective term referring to organisms which attach to a substrate in a flowing stream, composed mainly of algae and diatoms have been used as effective monitors of water quality. Cooper and Wilhm[41] used plexiglass plates suspended in a stream receiving domestic and oil refinery effluents to measure productivity, species diversity, and pigment diversity of colonizing periphyton. Comparison of the periphyton responses directly below the discharges and 60 km downstream indicated that species diversity was lowest near the outfalls and increased downstream. These data were interpreted as a measure of an improvement in water quality downstream from the outfalls.

Burks and Wilhm[31] used artificial substrates (Hester Dendy samplers) colonized with benthic macroinvertebrates from a nonpolluted stream as bioassay colonies. The authors demonstrated that species diversity, total number of species, and mean density of individuals could be used to evaluate the effects of an oil refinery wastewater during a 30-day exposure in artificial streams. In a comparison of an activated sludge treated, dual-media filtered, and activated carbon treatment methods, activated carbon treated wastewater caused no significant effects upon the benthic macroinvertebrate colonies. In contrast, the activated sludge treated wastewater caused a significant decline in species diversity, number of individuals, and mean density of individuals of the benthic macroinvertebrate colonies.

Burks[30] used the benthic macroinvertebrate bioassays and continuous-flow fathead minnow bioassays to evaluate the effectiveness of sequential pilot-scale dual-media filtration and activated carbon adsorption treatment technologies as "add on" systems to improve oil refinery wastewaters from biological treatment systems. The combined results of the fathead minnow and benthic macroinvertebrate bioassays clearly showed that activated carbon would remove toxic substances not removed by biological treatment systems. The range in median lethal time (LT_{50}) of fathead minnows to the biologically treated oil refinery effluents was from 11.5 hours to 28 days. The acutely toxic wastewater, i.e. LT_{50} = 11.5 hours, was from an activated sludge system which was hydraulically overloaded from rainfall runoff within the refinery. All of the other biological treatment systems were operating at near optimum efficiency. In seven tests performed at four different refineries, there were only two tests in which there was less than

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100 percent mortality of the test fish at the end of 32 days of exposure. Therefore, even though the effluents were not toxic in short-term exposures, the fish could not survive long-term exposures. Species diversity and total number of taxa of benthic macroinvertebrates were not as sensitive to the effluents as the fathead minnows. In three of the seven tests, there was no significant effect upon species diversity or number of taxa of benthic macroinvertebrates exposed to the biologically treated effluents for 32 days.

Another long-term effect of oil refinery wastewaters is an impairment of the taste/flavor of fish in the receiving waters. Studies initiated in 1952 and conducted intermittently until 1968 showed a direct relationship between the threshold odor number (TON) of oil refinery wastewaters and the presence of an "oily" taste/flavor of rainbow trout[96]. Dilutions of oil refinery wastewaters of greater than 1/100 were required to prevent occurrence of the "oily" taste/flavor in trout exposed to the effluent. A panel reported the odor was not like the odors of naphtha, turbo fuel or diesel fuel. Ogata and Ogura[132] exposed greenfish (Girella punctata) and eels (Angulla rostrata) to an aqueous solution of a mineral oil composed of 81 percent paraffinic and naphthenic hydrocarbons and 19 percent aromatic hydrocarbons. The taste and odor in the exposed organisms appeared to be caused by several unsaturated aliphatic hydrocarbons and possibly some aromatic compounds.

Steam volatile extracts of salmon collected from the Great Lakes contained over 85 different organic compounds identified by GC-MS. Many of the compounds were suspected to be derived from natural compounds synthesized by foodfish (alewives; 1-octen-3-one) or microbial activity (geosmin). However several of the compounds were suspected to have come from industrial waste discharges; p-methoxy thiophenol, naphthalene, 2-isopropyl phenol, 3-isopropyl phenol, 4-isopropyl phenol, t-butyl phenol, and chlorobenzaldehyde.

Several aquatic toxicologists have observed that behavior of aquatic organisms should be a very sensitive indicator of deleterious effects of chemical toxicants[162]. However, there have been very few studies of the effects of chemical pollutants upon behavior. A recently completed study at OSU indicates the utility of using changes in normal agonistic behavior of orange-spotted sunfish (Lepomis humilis) for detecting sublethal effects of oil refinery wastewaters. Agonistic behavior, aggressive acts such as bites and chases, is important in establishing territories and spawning areas of many fish. Exposure to non-lethal oil refinery wastewaters for periods of 10 days significantly decreased the agonistic behavior of the exposed fish compared to controls. The ecological significance of changes in agonistic behavior have not been determined yet, therefore the practical significance of these effects have yet to be demonstrated. However, such tests may be important for monitoring other more significant deleterious sublethal effects upon populations of organisms within receiving waters of oil refinery wastewaters.

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SECTION 5

AN EVALUATION OF EXISTING AND EMERGING CONTROL TECHNOLOGY FOR THE TREATMENT OF PETROLEUM REFINERY WASTEWATERS AND SLUDGES

Davis L. Ford
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INTRODUCTION

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Wastewater, spent acids, spent caustic, and other liquid materials are generated by petroleum refining operations and present disposal problems. The wastewaters emanating from refinery and petrochemical operations can be divided into five general categories:

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1. wastes containing a principal raw material or product resulting from the stripping of the material from solution;
2. reaction by-products;
3. spills, slab washdowns, vessel cleanouts, sample point overflows, etc.;
4. cooling tower and boiler blowdown, steam condensate, water treatment wastes, and general washing water; and
5. storm waters from contaminated drainage area[188].

The first consideration in the evaluation of treatment and control technology for a particular industry requires an estimation of the characteristics of the various source flows. A logical approach in formulating these estimates is to categorize the pollutional inputs into select source components. These components, as defined by Ford[189] are: (1) process operation wastes; (2) utility operation wastes; (3) sanitary sewage; (4) ballast water blowdown; and (5) contaminated storm runoff. The utility wastewaters include the blowdown from boiler and cooling systems. In addition, the miscellaneous flows resulting from spills, turnarounds, and other inordinate discharges also must be considered.

The principal contaminants in the wastewaters include organics from residual products and by-products, oils, suspended solids, acidity, heavy metals and other toxic materials, color, and taste and odor producing compounds. The principal parameters used to characterize organic wastewater constituents are BOD, COD, TOC, total oxygen

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demand (TOD), TSS, grease and oil, and phenolic compounds. The principal parameters used to characterize inorganic wastewater constituents are acidity, alkalinity, TDS, ammonia-nitrogen, sulfides, and specific inorganic ions. In many cases, it is important to measure the inorganic dissolved ions in solution such as chlorides, sulfates, nitrates, and phosphates. This is important in the quality control of cooling tower and boiler blowdown waters. The pH of refinery wastewaters is normally alkaline, but may vary considerably depending on disposal of spent acids, caustics, and acid washes.

PROCESS OPERATION WASTEWATERS

Wastewaters from plants manufacturing similar or even the same compounds usually display dissimilar characteristics. This can be ascribed to the use of different manufacturing processes coupled with the fact that the by-product disposal pattern may occur in a number of different ways. The many combinations of process operation, type of crude charge, or age of plant make classification of a "typical" refinery petrochemical wastewater difficult. The differences in in-plant effluent segregation systems, in-plant treatment systems, and process design, operation, and maintenance also contribute to these variations. The large variety of compounds produced within the refinery-petrochemical industry make the task of treating process wastewaters difficult and complex. Hence, a wastewater treatability study is often required before treatment options can be considered.

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The most common approach to predicting the quality of petroleum refinery wastewaters is to relate the quantity and quality of pollutant produced by a unit process to production[189, 190]. This information, when combined with general wastewater characterization data, offers insight into the nature of production and processing wastes. The principal processes which characterize the refining industry are: (1) crude and product storage; (2) crude desalting; (3) crude oil fractionation; (4) catalytic cracking; (5) thermal cracking; (6) hydrocracking; (7) reforming; (8) polymerization; (9) alkylation; (10) isomerization; (11) solvent refining; (12) dewaxing; (13) hydrotreating; (14) deasphalting; (15) drying and sweetening; (16) wax manufacture; (17) grease manufacture; (18) lubricating oil finishing; (19) blending and packaging; and (20) hydrogen manufacture. A brief discussion of the wastewaters and solid wastes associated with each of the aforementioned processes is presented herein.

The wastes associated with storage of crude oil and products are mainly in the form of free and emulsified oil and suspended solids. The storage of crude oil produces a waste liquor which is both high in COD and BOD and also high in an oily bottom sludge which must be removed intermittently. Crude oil storage is frequently the source of polysulfide-bearing wastewaters and suspended solids. Product storage can produce high BOD, alkaline wastewaters, as well as tetraethyl lead. Tank cleaning can contribute large amounts of oil, COD, and suspended solids, and a minor amount of BOD.

The wastes associated with crude oil desalting contain emulsified and free oils, ammonia, phenol, and suspended solids. The ammonia is added to the desalter to reduce corrosion. This waste stream is relatively high in BOD and COD, and contains

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significant levels of chlorides and other dissolved materials which contribute to the overall dissolved solids concentration in the combined wastewater. The temperature of the desalter waste often exceeds 200°F.

The wastes from crude oil fractionation generally result from the wastewater associated with overhead accumulators, the wastewater discharged from oil sample lines, and the wastewater associated with barometric condensers. The wastewaters from the accumulators are a major source of sulfides, especially when sour crudes are processed, and it also contains significant amounts of oil, chlorides, mercaptans, and phenols. The wastewaters characteristic of the barometric condensers which are used to create the reduced pressure in vacuum distillation units are a source of stable oil emulsions. Likewise, the major source of wastes in thermal cracking is the overhead accumulator on the fractionator. These wastewaters usually contain various oil fractions and may be high in BOD, COD, ammonia, phenol, and sulfides.

Catalytic cracking units are one of the largest sources of sour waters in a petroleum refinery. Pollution from catalytic cracking generally derives from the steam strippers and overhead accumulators on fractionators used to recover and separate various hydrocarbon fractions. The major pollutants resulting from catalytic cracking operations are oil, sulfides, phenols, and ammonia. These wastewaters are alkaline with high BOD and COD concentrations.

Information concerning waste production associated with hydrocracking has not been published; nevertheless, a waste stream from the process could be high in sulfides since hydrocracking reduces the sulfur content of the material being cracked. This waste stream would probably be generated in the product separation and fractionation units following the hydrocracking reactor.

Reforming, which is a relatively clean process, will generate a small volume of wastewater. This waste stream is alkaline, and the major pollutant is sulfide which is derived from the overhead accumulator on the stripping tower used to remove light hydrocarbon fractions from the reactor effluent. In addition to sulfides, the waste contains small amounts of ammonia, mercaptans, and oil.

Polymerization is characterized by a major pollution loading per barrel of charged material, but because of the small polymerization capacity in most refineries, the total waste production from the process is small. Even though the process makes use of acid catalysts, the waste stream is alkaline, because the acid catalyst in most of the subprocesses is recycled, and any remaining acid is removed by caustic washing. Most of the waste material, which is high in sulfides, mercaptans, and ammonia, comes from the pretreatment of the feedstock to the reactor. These materials are removed from the feedstock in caustic scrubbers and washwater towers. The spent caustic must be removed periodically and contributes to the solids disposal problem.

The two principal alkylation processes are cascade sulfuric acid alkylation and hydrofluoric acid alkylation. The general sources of waste in a sulfuric acid alkylation

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unit are the overhead accumulators in the fractionation section; the alkylation reactor; and the caustic wash. The wastewater from the overhead accumulators contains varying amounts of oil, sulfides, and other contaminants, but is not considered the major source of waste in this process. The waste from the reactor consists of spent acids and has a pH less than 3. This stream seldom enters the sewer system because most refineries process it to recover clean acids. Consequently, the major contaminants entering the sewer from a sulfuric acid alkylation unit are generally spent caustics from the neutralization of the hydrocarbon stream leaving the alkylation reactor. Hydrofluoric acid alkylation units do not have a spent acid or spent caustic waste stream; consequently, the major source of waste material is the overhead accumulator on the fractionator.

Data are not available concerning waste discharges from isomerization processes, but it is the general contention of the industry that these wastewaters are low in phenolic compounds and oxygen demand; and sulfides and ammonia are not likely to be present.

The potential pollutants from the various solvent refining processes are the solvents themselves. Many of the solvents used in the process, such as phenol, glycols, and amines, can produce a high BOD. Under ideal conditions, the solvents are continually recirculated; but in reality, some solvent is lost to the sewer through pump seals, flange leaks, etc. The principal source of wastewater is from the bottom of the fractionation towers. Oil and solvent are the major waste constituents. Likewise, leaks and spills are the major source of wastes in solvent dewaxing processes which use MEK. A spill of MEK can result in a waste stream which is high in BOD. Propane dewaxing is a cleaner process that poses few water pollution problems.

The hydrotreating process is used to saturate olefins, it also will remove sulfur, nitrogen, and oxygen compounds and other contaminants from either straight-run or cracked petroleum fractions. The strength and quantity of waste generated by a hydrotreating process depends on the type of process used and the material being hydrotreated. The major waste streams derive from overhead accumulators on fractionators and steam strippers and sour water stripper bottoms. The major pollutants are sulfides and ammonia. Phenols also may be present if the boiling range of the feed is high enough.

Data are not available concerning waste discharges from deasphalting processes. Indications are that wastewater does not result from the actual deasphalting step, but is generated from overhead condensers on the steam strippers that are used to separate the asphalt, deasphalted oil, and propane. This "sour water" generated from the condensers probably contains small amounts of sulfides, oil, and ammonia.

The principal waste stream from drying and sweetening operations is spent caustic. The spent caustic is characterized as phenolic or sulfidic depending on which is present in the largest concentration. Phenolic spent caustics contain phenol, cresols, xylenols, sulfur compounds, and some neutral oils. Sulfidic spent caustics are rich in sulfides, but do not contain any phenols. Both spent caustics are usually high in BOD and COD. Other waste streams from the process are generated from water washing of the treated product and regeneration of the treating solution. These waste streams will

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contain small amounts of oil and the treating material; namely, sodium plumbite or copper chloride.

Data are not available concerning waste discharges from wax manufacturing processes, but there is little reason to believe that such wastes pose a significant source of pollution. Likewise, only small volumes of wastewater are discharged from grease manufacturing processes. In the case of both manufacturing processes, a small amount of oil may be lost to the wastewater system through leaks; but the largest waste loading occurs when batch units are washed. This results in soap and oil discharges to the sewer.

Acid treatment of lubricating oils produces acid-bearing wastes occurring as rinse waters and sludges. In addition, there are discharges from sampling points, leaks, and shutdowns. These waste streams are usually high in dissolved and suspended solids, sulfates, sulfonates, and stable oil emulsions. The acid sludges produced in this process create a significant solids handling problem.

Blending and packaging processes pose few pollution problems because care is taken to avoid loss of product through spillage. The primary source of waste material is from the washing of railroad tank cars or tankers prior to loading finished products. These wash waters are high in emulsified oil. Sludges from gasoline storage tanks can contain large amounts of tetraethyl lead, a highly toxic compound, which could be flushed into the wastewater system during washing operations.

Information concerning wastes generated during hydrogen manufacture is not available; however, the process appears to be relatively clean. In the special case of the steam reforming process, a potential waste stream produced during desulfurization would contain oil, sulfur compounds, and phenol.

UTILITY OPERATION WASTEWATERS

Utility operations which are an integral part of a petroleum refinery contribute to the wastewater flow in the form of blowdown from boilers, process steam generators, and cooling towers. In order to control excessive scaling and fouling of heat transfer surfaces in boilers and process steam generators, a limitation is placed on the level of dissolved solids and alkalinity present in the water within steam drums. Blowdown occurs each time treated makeup water is fed to the system so that allowable quality limits can be maintained. Although the volume of process steam generation blowdown will vary from system to system, it normally represents less than 5 percent of the total treated feed water used to produce steam. This is a small portion of the total utility operation wastewater volume; although, the concentration of key water-quality constituents may be significant. Blowdown from cooling towers represents a sizable portion of the combined wastewater flow, and constitutes the majority of the utility wastewater volume.

In general, cooling tower effluent quality will be similar to the feed water supply for a once-through cooling system except for the addition of corrosion control chemicals. Cooling towers which recirculate water within the system experience higher

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salt concentrations since pure water is continuously evaporated to the surroundings. Cooling tower additives, TDS, and contaminants entering the water through heat exchanger leaks constitute the pollution characteristics of cooling tower blowdown. The most commonly used additives for corrosion and algae control are chromates and phosphates.

Boiler and cooling tower blowdowns which are segregated from process wastewaters are sometimes referred to as clean streams. Such nomenclature is predicted on the relative organic content of the waste stream and only is valid if the segregation of stream rigidly follows process-utility operation lines. However, utility blowdown streams still contain organic pollutants; albeit, at low concentrations. The principal clean stream quality parameters are TDS, temperature, chromates, phosphates, and pH.

CONTAMINATED STORM RUNOFF

Storm runoff is a high volume, intermittent wastewater stream which is both quantitatively and qualitatively unpredictable. The flow rate and contaminant concentration will not only vary with time during the course of a storm, but also will change with each individual area within a refinery-petrochemical complex since each area has its own geometric characteristics which influence patterns of surface runoff. The investigation of storm water flows is usually oriented toward obtaining data regarding the probable wastewater volume, quality characteristics, and runoff hydrograph shape. The anticipated rainfall volume estimate is developed statistically from long-term precipitation records with sufficient accuracy to allow computation of meaningful probability statements concerning future events.

The character of contaminated storm runoff is similar in water quality to the wastewaters generated during operation of the petroleum refinery inasmuch as there will exist a significant oxygen demand, TSS, and oil and grease level in the runoff which must be removed before these waters can be discharged to a receiving body. The analysis of storm flow COD concentration relationships from numerous refinery-petrochemical complexes has indicated that between 60 and 80 percent of the organic mass is washed from the surface of the facility during the first hour of the rainfall-runoff event[189]. Similar relationships exist for other pollutant constituents.

BALLAST WATER BLOWDOWN

Tankers and barges which transport crude or products to and from refinery and petrochemical facilities in coastal areas seldom carry payload on both legs of a journey. This is true of refineries in crude-producing areas where tankers are used primarily for exporting finished products. Consequently, the excess ballast from incoming tankers is discharged at the debarkation port.

WATER POLLUTION CONTROL MEASURES IN PETROLEUM REFINING

Isolation of liquid wastes at their source for treatment before discharge of the

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water to the refinery wastewater collection system has been found to be the most effective and economical means of minimizing pollution problems. Among the principal wastes that could be treated separately are oil-in-water emulsions, sulfur-bearing waters, acid sludges, and spent caustic wastes. A complete evaluation of the effectiveness of in-plant processing practices in reducing wastewater pollution requires detailed information on the wastewater flows and pollutant concentrations from all types of refinery process units and storage facilities. Unfortunately, this kind of information is not readily available.

Despite the lack of specific process wastewater data, there exists information of a more general nature which indicates that substantial wastewater pollution reduction could be achieved through changes in processing facilities and practices. For instance, hydrocracking and hydrotreating are two processes that generate much lower waste loadings than the processes they replace. However, the greatest potential for in-plant waste load reduction appears to be in improvement of general operating and housekeeping practices rather than in changing processes or subprocesses.

Although the central thrust of this treatise is to evaluate existing and emerging end-of-pipe wastewater treatment technology as it applies to the petroleum refining industry, one should be aware of the existence of numerous in-plant source reductions, process modifications, and control practices which contribute to the overall goal of pollution control. Such in-plant treatment control methods include stripping and recovery operations, neutralization and oxidation of spent caustics, ballast water treatment, slop oil recovery, and temperature control. These assorted in-plant treatment practices not only reduce the waste loadings to the wastewater treatment facility, but also enhance its performance. In some cases, in-plant control will show a cost credit in the form of product recovery.

Oil-Water Separation

Oily wastewater treatment systems are found in the three phases of the petroleum industry; namely, production, refining, and marketing. These systems will vary in size and complexity, although their basic function is to collect and recover valuable oils and to remove undesirable contaminants before discharge to a receiving body. The wastewater treatment systems found in refineries are larger and more elaborate than those found in the production phase. The wastewater collection system of a modern refinery usually includes gathering lines, drain seals, junction boxes, and channels of vitrified clay or concrete which transport wastewater from processing units to oil-water separators. These oil-water separators are designed to receive wastewater from all process sources, sometimes even including storm runoff and ballast water blowdown. The discharge of liquid wastes to these systems originates from a variety of sources such as pump gland and accumulator leaks, process spills, cleanouts, sample ports, relief valves, etc.

The removal of oil contamination from wastewaters can be accomplished by the use of several well-known and widely accepted techniques. The performance of any given separation technique will depend entirely on the condition of the oil-water mixture;

therefore, the nature of a particular oily waste stream must be determined before the proper treatment device can be selected. The types of oil-water mixture which can be encountered may be classified as wastewaters with oil present as free oil, dispersed oil, emulsified oil, and dissolved or soluble oil. Free oil is usually characterized by an oil-water mixture with droplets larger than 150 microns in size, while a dispersed oil mixture will have a droplet size range between 20 and 150 microns. An emulsified oil mixture will have droplet sizes smaller than 20 microns. A wastewater which is characterized by an oil-water mixture where the oil is said to be soluble, is a liquid waste where oil is not present in the form of droplets. Soluble oils are, in actuality, nonoily materials such as phenolic type aromatic compounds and colloidal sulfur compounds which are selectively extracted to varying degrees by the solvents used in the analysis.

Several professional societies and industrial institutes have offered definitions for oil in the form of methods for measuring oil concentration in water and wastewater. The commonly used solvents in oil and grease analysis are hexane, petroleum ether, benzene, chloroform, carbon tetrachloride, and freon. These solvents exert selective extraction of specific greases and oily constituents. Since oily matter and grease may be of mineral, animal, or vegetable origin, the solvent action, exerted on material of such different chemical structure, will vary to a marked degree. The application of a test method for oil and grease analysis to such material will produce a variety of results each depending on the solvent used. Therefore, the definition of grease and oily matter is, by necessity, based on the procedure used for analysis.

Theory and Practice of Gravity Oil Separation

The three main forces acting on a discrete oil droplet are buoyancy, drag, and gravity. The buoyancy of an oil droplet is proportional to its volume and the drag is proportional to the projected area of the droplet. As the diameter of an oil droplet decreases, the ratio of its volume to surface area also decreases. Because of this droplet size relationship, larger droplets tend to rise while smaller droplets remain suspended. This relationship is defined by the well-known "Stokes Law." The concept assumes that the terminal velocity of a rising droplet is: (1) proportional to the specific gravity difference between the oil and water; (2) proportional to the square of the oil droplet diameter; and (3) inversely proportional to the viscosity of the water.

The oil removal efficiency exhibited by a particular separator is a function of the droplet size distribution, the amount of oil present in the contaminated water, and the presence of surfactants or chemical emulsifiers which may or may not be indigenous to the crude oil.

If a free or dispersed oily water mixture is brought to a relatively quiescent state and given sufficient time, the oil droplets will coalesce and eventually separate from the wastewater. The droplets which collect on the surface of the water will coalesce, primarily because of their proximity to other droplets, and form a continuous floating oil layer which may be decanted from the water. This process is called "gravity separation."

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Generally, oil droplets 20 microns and smaller cannot be separated practically with a gravity separator because the net buoyancy force is overcome by the drag force of the continuous water phase. These droplets which were previously classified as emulsified oils are so small that the random movement of the water keeps them suspended. In addition, impurities present in both the oil and water phases also may affect the separability.

Nearly all oily wastewaters have some amount of free, dispersed, and emulsified oil present. Rainfall runoff which has not been pumped may typically be contaminated with oils which have between 8 and 10 percent of the oil droplet sizes below 20 microns. Pumped mixtures may have up to 20 percent of the oil droplets below microns. Contaminated bilge and ballast water will typically have from 10 to 15 percent or more of the oil in a mechanically emulsified state.

The principal objective of gravity differential-type oil-water separators such as the API separator and the parallel or tilted-plate separator is to establish an environment in which suspended solids are settled coincident with the separation of oil in the influent. The current design principles of the API separator are based on extensive studies into the effect of inlet and outlet arrangements on oil separation efficiency as well as the impact of appurtenances on the hydraulic characteristics in the separation chamber. The principal factors which affect the design of oil-water separators are: (1) the specific gravity of the oil; (2) the specific gravity of the wastewater; (3) wastewater temperature; (4) the percentage of emulsified oils; and (5) the concentration of suspended solids. The specific gravities of both oil and water which are a function of temperature determine the rate of oil separation. The aforementioned factors set the allowable hydraulic overflow rate for the particular oil-water separator design.

The parallel-plate interceptor (PPI) separator essentially reduces the distance that a particle of oil must travel before reaching a collection surface. In this case, such a surface consists of a number of parallel plates, evenly spaced and set at an angle from the horizontal. The oil particles coalesce on the underside of these plates and creep up to the water surface. Therefore, the distance traveled by an oil droplet is a few inches instead of several feet. An alternate design uses a variant of the normal PPI separator known as the tilted-plate separator (TPS) or the CPI which have only recently been applied to the removal of free oil from refinery effluents.

A coagulation-flocculation step is commonly employed in refinery wastewater treatment to increase the overall removal of oil and suspended solids. The flocculated suspension may be removed by simple gravity separation but an air flotation scheme is more common. The addition of a chemical coagulant to an oil contaminated wastewater serves to promote the aggregation of dispersed and emulsified droplets into flocculated clusters. It also may negate the effects of indigenous crude oil surfactants and permit smaller droplets to coalesce into larger ones. This process is irreversible, leading to a decrease in the number of oil droplets and finally to complete demulsification. The net effect of coagulation-flocculation is to render the suspension more amenable to phase separation.

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When a quantity of an aluminum (Al^{+++}) or iron (Fe^{+++}) salt sufficient to exceed the solubility limit of the metal hydroxide is added to water, a series of complex hydrolysis reactions occurs. These proceed from the production of simple hydro-complexes through the formation of a metal hydroxide precipitate. The reactive form of these complexes is a function of system kinetics, expressed as metal ion concentration, pH, and alkalinity. Chemical theories attribute coagulation to precipitation of metal hydroxides which act to enmesh colloidal particles, specific chemical reactions, surface adsorption, and specific chemical interactions involving coagulant hydrolysis products.

The impact of coagulation-flocculation on removal of emulsified oils is represented by the data presented in Figure 9. These data indicate the results of a series of batch tests conducted to examine the means by which aluminum added as alum and iron added as ferric sulfate interact with oil droplets[191]. The curves presented in Figure 9 reveal that performance response is a strong function of pH. The factors believed to be responsible for the oil removal at pH=5.5 and 8.5 are the charge on the oil droplet and the nature of the hydroxy-metal species. The combined effects of charge reduction, sorption to the droplet surface, and interdroplet bridging are required to effect significant oil removal.

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Synthetic organic polymeric electrolytes or polyelectrolytes are used with increasing frequency in water and wastewater treatment. They function both as primary coagulants and as coagulant aids when used in conjunction with metal coagulants. As a coagulant aid, their principal function is to strengthen the flocs formed by metal coagulants such as alum. A series of batch tests was conducted in order to examine the effects of polyelectrolyte addition on oil removal efficiency and these data are presented in Table 11[191]. Specific factors evaluated were polymer type (anionic, nonionic, or cationic), polymer dose, and order of addition. The data presented in Table 11 indicate that the anionic polymer is least effective for oil removal and that the nonionic and cationic varieties are approximately equal. However, none of the polyelectrolytes examined resulted in sufficient oil removal to justify its use as a primary coagulant.

Since both the polyelectrolytes and the oil droplets are highly charged, there exists a very strong electrostatic attraction between the two substances. Consequently, this may result in a nonspecific interaction in which the polymer coats the oil droplet surface instead of attaching at a point and extending into solution to act as a bridging agent for other droplets. Moreover, the relatively high ionic strength of petroleum refinery wastewaters may inhibit the polymers from fully uncoiling in solution, thereby reducing their effectiveness.

These same polyelectrolytes were evaluated as coagulant aids in conjunction with alum as the primary coagulant. The results of these tests are presented in Figure 10 and indicate that polymer addition does not significantly improve oil removal efficiency but may even hinder it[191].

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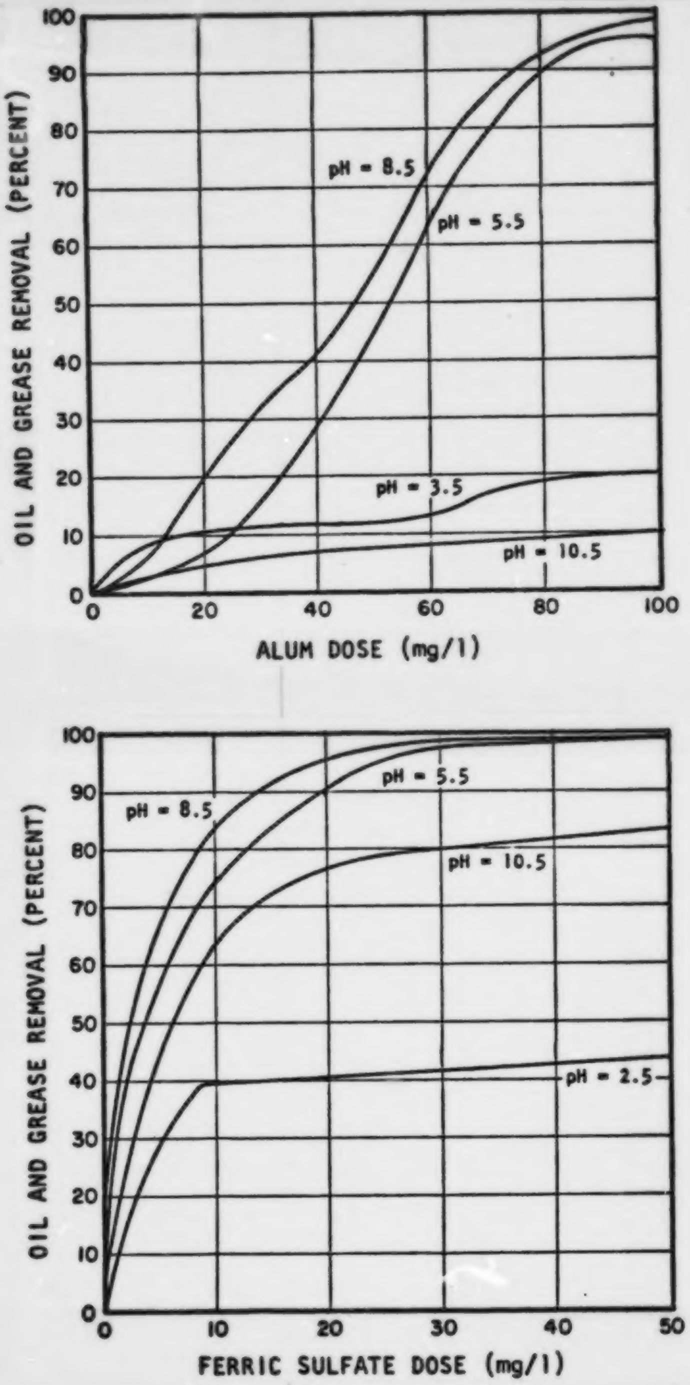

NOTES;

INITIAL OIL AND GREASE = 200 mg/l

DILUTE EMULSION 10-25 MICRONS DROPLET DIAMETER

TDS = 2,700 mg/l

ALKALINITY = 500 mg/l as $CaCO_3$

FIGURE 9. Experimental observations concerning oil and grease reduction with coagulant addition

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TABLE 11. POLYELECTROLYTES AS PRIMARY COAGULANTS FOR CRUDE OIL DISPERSIONS

Polyelectrolyte Dose (mg/l)	Percent Oil and Grease Removal		
	Anionic Polymer*	Nonionic Polymer**	Cationic Polymer***
0.1	16	23	18
0.2	15	20	27
0.5	16	26	27
1.0	15	29	30
2.0	12	29	29
5.0	12	27	31
10.0	10	27	31

*Anionic polymer = polystyrene sulfonate, approximate molecular weight 2 x 10^6.

**Nonionic polymer = polyacrylamine, approximate molecular weight 1 x 10^6.

***Cationic polymer = polyacrylamide, approximate molecular weight 1 x 10^4.

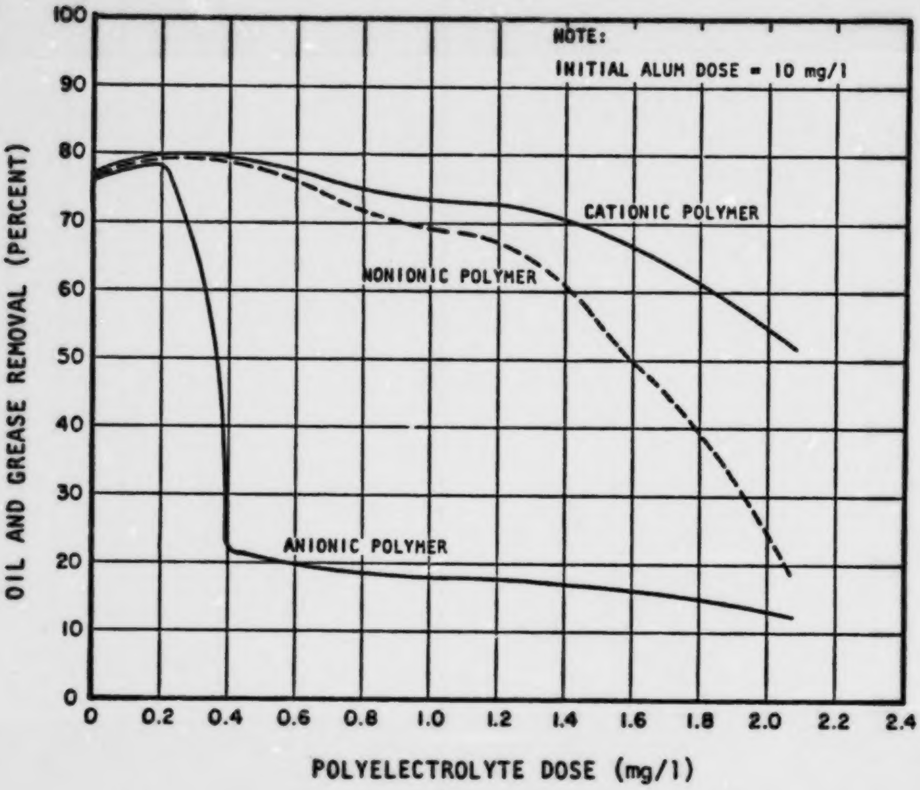

FIGURE 10. Polyelectrolytes evaluated as coagulant aids in conjunction with alum as the primary coagulant

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Flotation Oil-Water Separation

Flotation is one of the most common oil refinery wastewater pretreatment techniques and generally includes a chemical coagulation-flocculation step. It is a unit operation specifically designed for the separation of liquids and solids from wastewater. Natural flotation occurs to some extent in gravity oil-water separation techniques, but is generally limited to the removal of oil globules greater than 40 microns in size.

The flotation process relies on uniting gas bubbles with the dispersed oil phase resulting in a reduction in the specific gravity of the oil and a subsequent increase in rise velocity. Flotation is strongly influenced by the surface characteristics of the dispersed oil phase and to a lesser degree by the oil droplet size.

Flotation methods are divided into dispersed-gas and dissolved-gas processes. Dispersed or entrained gas flotation utilizes bubbles generated by one of the following techniques: (1) mechanical shear; (2) gas diffusion through a porous media; or (3) homogenization of the gas into the wastewater. Dissolved gas flotation generates gas bubbles by the precipitation of gas from a super-saturated solution. The processes differ in the size of the gas bubble produced. In dissolved gas flotation, bubbles average 80 microns in diameter, while they are generally an order of magnitude larger in dispersed gas flotation. The gases commonly used for flotation of dispersed oils are air and nitrogen. Air will oxidize any ferrous iron in the wastewater which may precipitate as ferric hydroxide. The ferric hydroxide, however, may act as a coagulating agent and improve overall oil removal efficiency.

DAF is the process commonly used in refinery and petrochemical installations to enhance oil and suspended solids removal. It is generally preceded by a gravity oil separator which will remove gross quantities of free oil and oily suspended solids. The process involves the pressurization of wastewater in the presence of air, thereby creating a super-saturated solution which when passed into a flotation chamber at atmospheric pressure will precipitate the air from solution in the form of small bubbles. These bubbles unite with the dispersed oil phase to form a collection of distinct oil droplets (coagule) and carry it to the surface. The float is removed to disposal or recovery by mechanical flight scrapers, while the underflow represents the clarified effluent.

The mechanisms by which the air bubbles and dispersed oil droplets interact are generally classified as follows: (1) the adhesion of oil droplets to air bubbles; (2) entrapment of air bubbles in a coagule or a flocculant structure; and (3) absorption of air bubbles into the coagule or floc structure.

The principal modes of operation for the DAF process are: (1) full wastewater stream pressurization; (2) split stream pressurization; and (3) recirculation stream pressurization. Most applications of the DAF process for the treatment of refinery wastewaters use recycle stream pressurization as the principal mode of operation. This system has the advantage of requiring a smaller pressurizing pump than in full-stream pressurization so that capital and operating costs are reduced. In addition, pump life is increased because

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abrasive solids are not pumped since they are separated from the recycle stream in the flotation chamber prior to pressurization. Flocculant structures formed in the wastewater stream are not subjected to the shearing forces of the pressurization pump. Moreover, emulsion formation due to shear is minimized. A potential disadvantage of recycle operation as compared to full-stream or split-stream operation is the necessity of an enlarged flotation chamber.

The use of chemical agents has historically been an integral part of the flotation process. These chemicals function by modifying the surface properties of one or more phases. For instance, there are chemical agents (frothers) which serve to lower the interfacial tension between the air bubble and the wastewater. Other chemical agents (collectors) either reduce the interfacial tension between the dispersed oil phase and the wastewater or increase the interfacial tension between the air bubbles and the oil phase. Both conditions tend to increase bubble-droplet adhesion. Coagulating chemicals such as aluminum and iron salts are often used to enhance the bubble capture mechanisms of flotation. As discussed previously, these coagulants function to improve the flocculant nature of the dispersed oil phase and enhance the capture of small oil droplets.

The coagulants may be introduced into the process stream in many ways depending on the mode of operation and the type of chemicals used. In some installations, the chemical is injected downstream of the pressure release; while at others, it is injected directly into the suction side of the pressurizing pump. When chemicals are injected directly into the pressurizing pump suction, mixing is enhanced; but the relatively short time available for floc formation along with the shear forces encountered may be detrimental to the overall system performance.

In recycle or split flow operation, the coagulant may be added directly to the wastewater in a separate reactor for better control of the coagulation-flocculation process. The flocculated wastewater stream is then transferred by gravity to the flotation chamber where it is combined with the pressurized stream. This mode of operation provides for more effective use of coagulants by increasing reaction time as well as improving floc formation and increasing separation rates.

Oil-Water Separator Performance

Oil-water separator treatment efficiency is a function of many design and operating variables. The two factors which are most significant in impacting upon separator performance are flow rate and influent oil concentration. Separators must be protected in order to prevent flushing during periods of high flow. Bypass and overflow lines generally are used to provide this hydraulic protection. The influence of initial oil and grease concentration on the treatment performance of conventional oil-water separators is illustrated in Figure 11. Assuming the systems are operated properly, these data indicate that the influent oil concentration is a significant factor with respect to process capacity and efficiency. This effect is underscored by data for both the conventional API separator and the chemical flocculation DAF unit inasmuch as higher influent oil concentrations are removed with greater efficiency than that of low influent oil concentrations.

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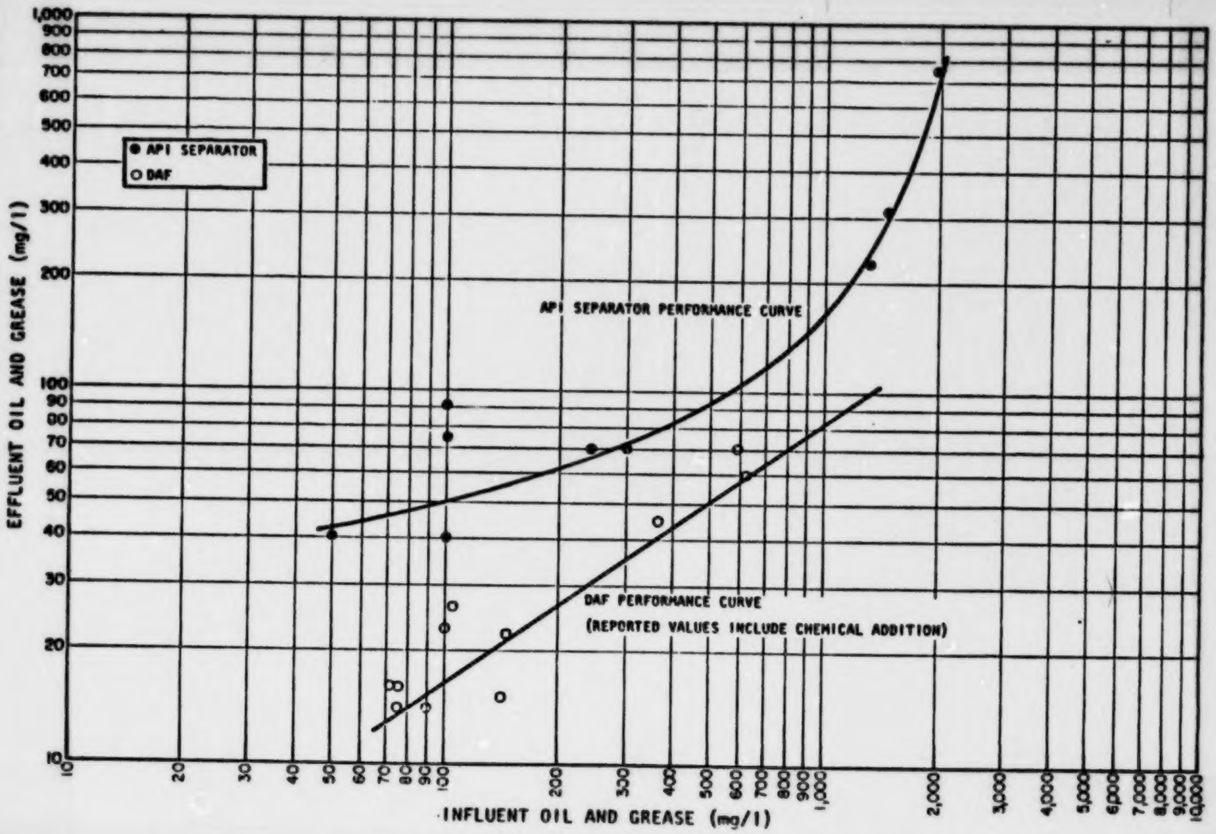

FIGURE 11. Impact of influent oil and grease concentration on treatment performance of conventional oil-water separators.

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Although gravity separation will not provide a satisfactory effluent oil quality for direct discharge to biological treatment, it is the most economical and efficient approach to the removal of high concentrations of incoming free oil. The effluent oil concentrations from API separators generally range from 70 to 150 mg/ℓ, although deviations on either side of this range are common due to the great variety of wastewaters treated with this type of oil removal equipment. Nevertheless, under excellent operating conditions, an apparent lower limit of oil in a gravity separator effluent is usually around 50 mg/ℓ. It should be emphasized that the removal efficiency of all gravity separation techniques is a function of temperature and the density difference between oil and water.

As observed from the data presented in Figure 11, DAF unit effluent oil levels of 10 to 30 mg/ℓ can be achieved if the influent oil concentration remains below 200 mg/ℓ. Although it is possible to obtain an effluent oil quality of 10 mg/ℓ under certain conditions with a chemical flocculation DAF unit, consistent performance at a 10 mg/ℓ effluent oil concentration would appear to be difficult if not impossible to sustain[192]. This is particularly true when considering the fluctuations in influent oil concentration inherent with most petroleum processing operations, and the corresponding effect on gravity and DAF oil removal systems.

The effect of peak hydraulic loading on API separator effluent oil concentrations is illustrated by the data presented in Figure 12. In general, the ideal API separator design seeks to limit the extent to which turbulence and short-circuiting will affect the operation of the separator. The effects of turbulence increase with the magnitude of the ratio of the horizontal velocity to the rate of oil droplet rise. Theoretically, turbulence only can be compensated for by decreasing the overflow rate. It is apparent from the data presented in Figure 12 that a deterioration of effluent oil quality will occur when hydraulic surges exceed the design maximum. Unfortunately, a theory does not exist which defines the magnitude of a maximum absolute value of the horizontal velocity.

Data collected during the operation of a pilot-scale tilted-plat separator are presented graphically in Figure 13. The pilot unit was operated as part of a comprehensive treatability study on wastewaters from an integrated petroleum refinery. The apparent oil removal efficiencies tend to vary between a low of 50 percent to a high of 80 percent at the design average hydraulic load. Like the API separators, the treatment performance of the TPS unit is affected by hydraulic surges, and the overall suspended solids and oil removal efficiency of this pilot unit did decrease when the system was operated at 1.5 times the design average hydraulic load. Nevertheless, there is broad application for tilted-plate separators in the treatment of refinery-petrochemical wastewaters since so little space is required for their installation. The TPS unit can be installed in series with an existing API separator which is either overloaded or improperly designed, thereby increasing the overall oil removal efficiency normally obtained by this gravity separator. The TPS unit also can be installed to operate in parallel with existing API separators, reducing the hydraulic load and enhancing the oil removal capacity of the system.

Several case histories where DAF units are used to treat refinery oily wastewaters are presented in Figures 14 and 15. These curves represent statistical analyses of

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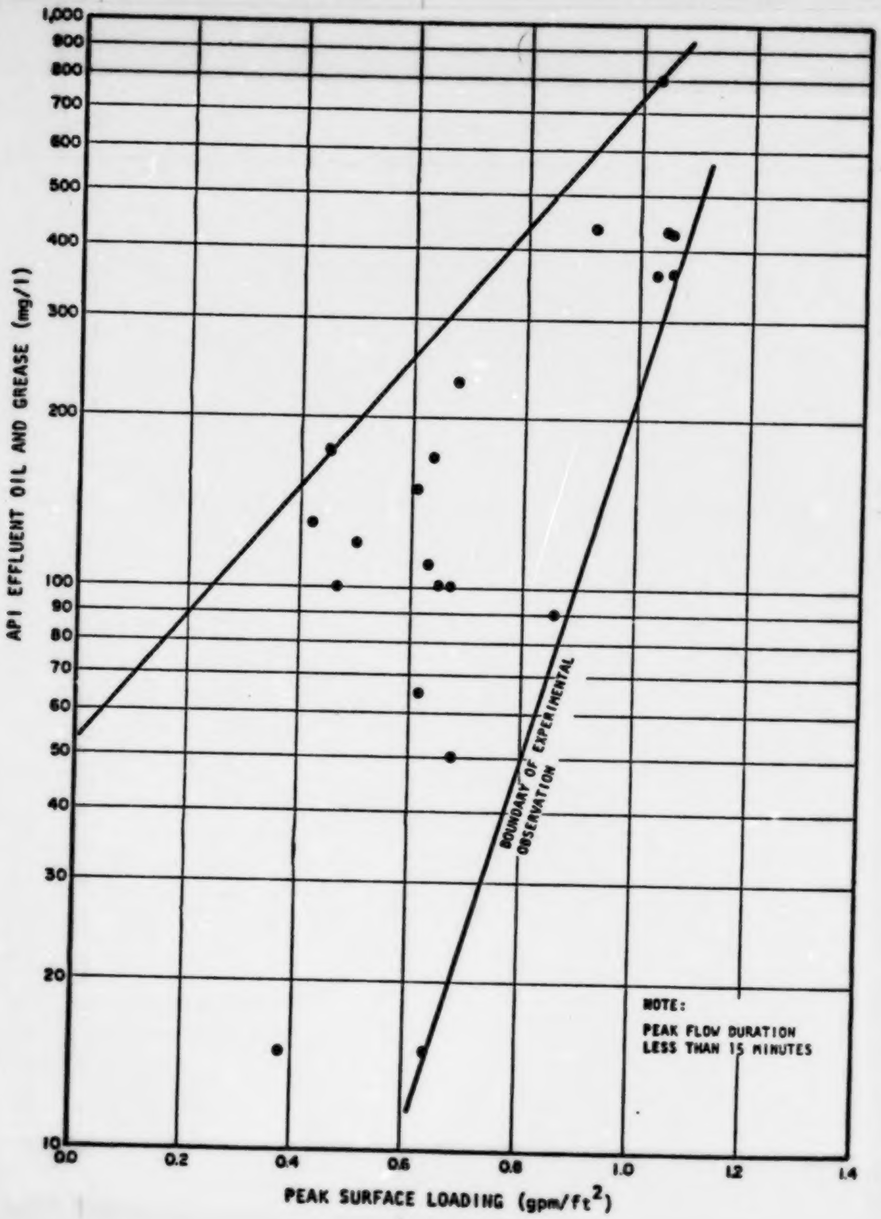

FIGURE 12. Impact of peak hydraulic loading on API separator effluent quality.

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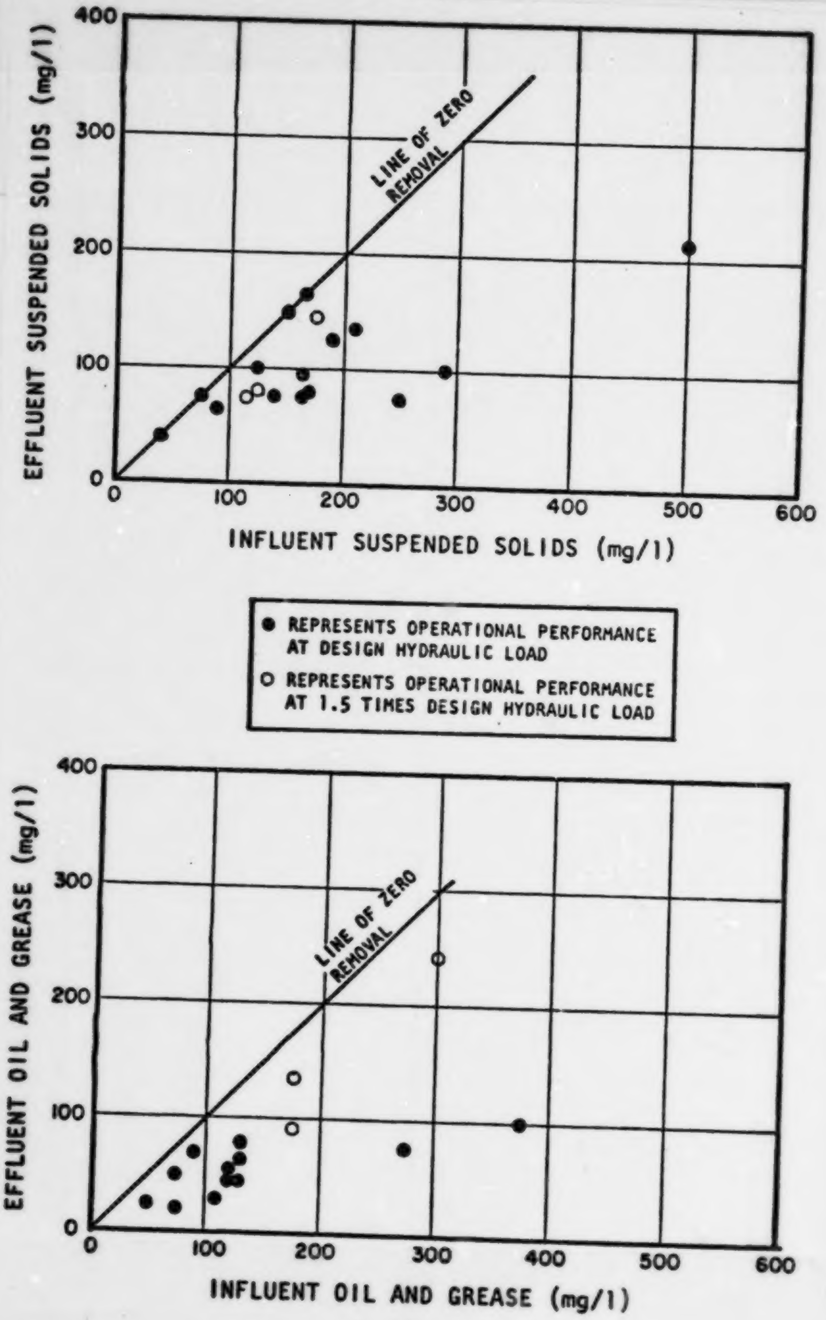

FIGURE 13. Treatment performance of pilot-scale tilted-plate separator

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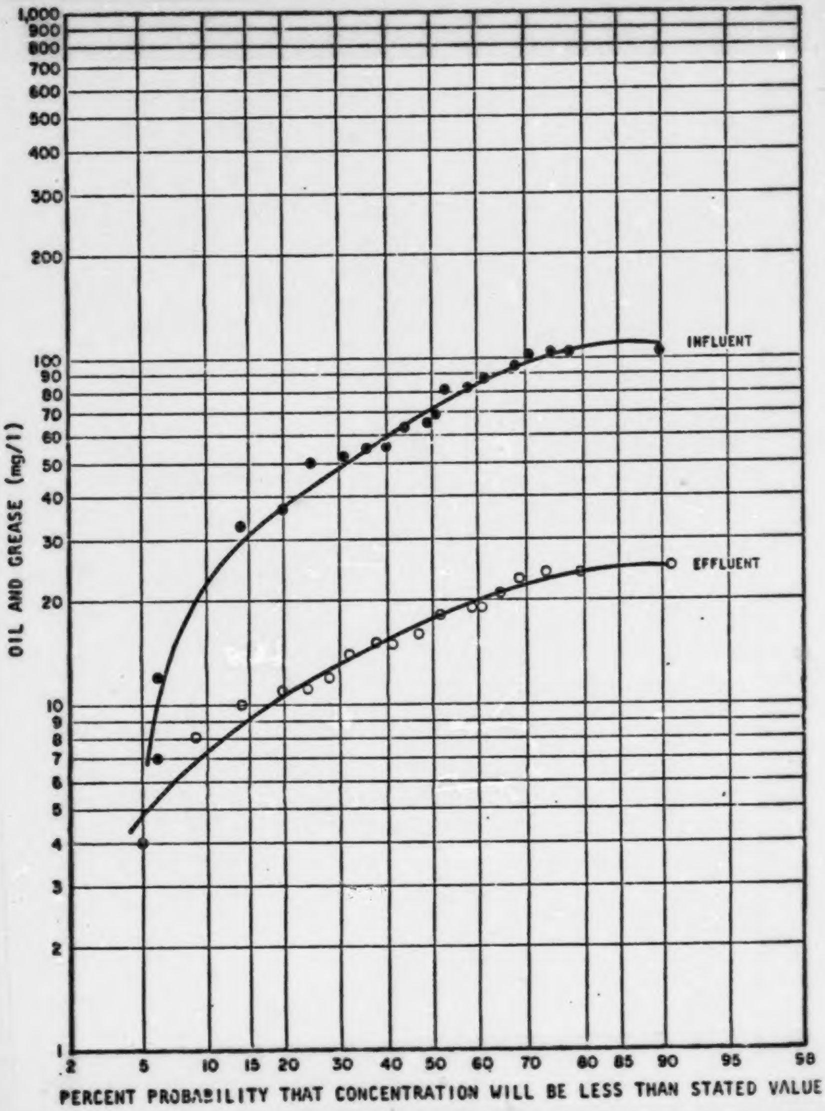

FIGURE 14. Variation in DAF treatment performance for oil and grease removal.

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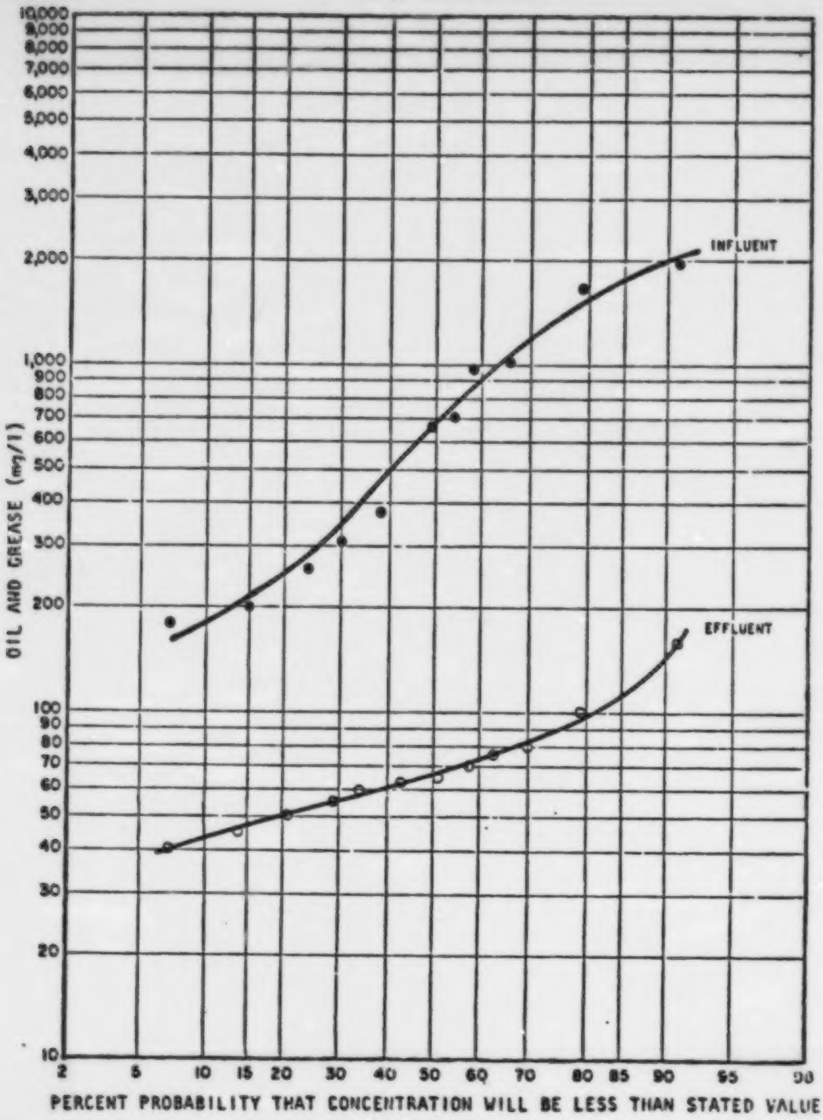

FIGURE 15. Variation in DAF treatment performance for oil and grease removal.

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DAF process efficiency data obtained from wastewater surveys performed within petroleum refineries which employ flotation oil-water separation equipment for secondary oil recovery. The first case history which is graphically presented in Figure 14 is characteristic of the expected treatment performance associated with a DAF unit operated in series with an API separator. These data indicate that the DAF unit reduced the oil level from 68 mg/ℓ to 15 mg/ℓ 50 percent of the time, and from 105 mg/ℓ to 25 mg/ℓ at a 90 percentile probability level. The second case history (Condition B) which is presented in Figure 15 depicts the variation in DAF treatment performance for oil and grease removal at a much higher level of influent concentration. These data indicate that this DAF unit reduced the median oil level from 580 mg/ℓ to 68 mg/ℓ and the 90 percentile probability value from 1,930 mg/ℓ to 128 mg/ℓ.

DAF oil removal efficiency is a function of many factors; namely, design overflow rate, retention time, recycle volume, pressurization level, air-to-solids ratio, type and volume of chemical addition, and the concentration and form of the influent oil. The data tabulated in Table 12 account for these variables inasmuch as the operational overflow rates fall within the accepted design spectrum of 1.5 to 3.0 gallons per minute (gpm) per square foot and all use the pressurized recycle mode of operation. All of the cases cited use coagulation-flocculation with the principal chemical being alum at a dosage of between 100 and 150 mg/ℓ on the average. A few operate with a small polyelectrolyte addition.

In general, the DAF unit experiences better oil and grease removal at the higher influent concentration levels. This also is the case regarding the separation of influent suspended solids and COD. The overall COD removal efficiencies presented in Table 12 are not surprising when one considers that a large fraction of the COD is associated with suspended solids.

The information presented in Table 13 summarizes the design parameters which characterize full-scale DAF units treating petroleum refinery wastewaters both with and without coagulant addition. It should be emphasized that air flotation without chemical addition is not widely used in refinery wastewater treatment. Moreover, the addition of polyelectrolytes has not substantially increased oil-water separation by air flotation systems to warrant their use as anything other than a coagulant aid. This is indicated by the data presented in Figure 16 which depicts air flotation process efficiency as a function of influent oil concentration. The data specify treatment performance of both DAF units and induced air flotation (IAF) units with various ranges of polyelectrolyte addition. It is apparent from these data that polyelectrolyte addition did not improve flotation treatment efficiency, and in some cases, it may have even hindered effective oil removal.

The variation in the treatment performance of a pilot-scale IAF unit used primarily for oil-water separation is presented in Figure 17. Pollutant removal efficiencies are essentially equal to those achieved by the DAF units, but operation is more difficult and chemical flocculant requirements are significantly higher. Moreover, the skimmings are much less concentrated and represent a significant waste solids disposal problem.

TABLE 12. EVALUATION OF DISSOLVED AIR FLOTATION TREATMENT PERFORMANCE

Sample Observation	Oil and Grease Removal: Influent (mg/l)	Oil and Grease Removal: Effluent (mg/l)	Oil and Grease Removal: Percent Removal	COD Removal: Influent (mg/l)	COD Removal: Effluent (mg/l)	COD Removal: Percent Removal	TSS Removal: Influent (mg/l)	TSS Removal: Effluent (mg/l)	TSS Removal: Percent Removal
1	1,781	20	99	1,335	492	63	740	86	88
2	2,029	35	98	4,115	552	87	1,304	48	96
3*	1,034	50	95	2,813	-	-	650	36	94
4	3,500	54	98	4,525	1,125	75	805	170	79
5	700	60	91	1,660	656	60	244	41	83
6*	970	160	84	1,680	615	63	229	27	88
7	1,530	73	95	3,663	555	85	466	50	89
8	230	60	74	793	453	43	75	32	57
9*	420	190	55	1,200	675	44	152	121	20
10	720	130	82	4,432	1,968	56	222	106	52
11	310	90	71	4,702	2,551	46	115	34	70
12	324	72	78	986	513	48	142	77	46
13	170	70	59	966	523	46	95	70	26

*Addition of five mg/l polyelectrolyte.

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TABLE 13. DISSOLVED AIR FLOTATION DESIGN PARAMETERS

Design Parameter	Example Refinery							
	A	B	C	D	E	F	G	H
Average Inlet Oil and Grease, mg/l	-	270	70	112	-	-	100	125
Hydraulic Loading Rate, gpm/ft^2	3.5	2.3	2.9	2.3	4.0	2.5	2.9	2.3
Detention Period, minutes in flotation chamber	19.5	23	27	20	10	25	-	-
Recycle Pressure, psig	50	40	40	45	40	40	-	-
Recycle, Percent of Feed	25	33	33	see note	50	35	25	see note
Air-Water Ratio, SCF/100 gal	0.8	1.0	1.0	0.36	-	1.0	-	-
Chemical Addition prior to Flotation	Yes	No	Yes	Yes	Yes	Yes	Yes	No
Inlet pH	-	-	-	6.5-10.0	8.5-10.0	-	-	-
Design Flow, mgd	30	4.3	5.7	2.5	2.5	-	-	-
Oil Removal Efficiency, Percent	70-85	60	92	66	75	-	92	72
Suspended Solids Removal Efficiency, Percent	30-50	-	72	-	-	-	-	-

NOTE: Full flow pressurization method.

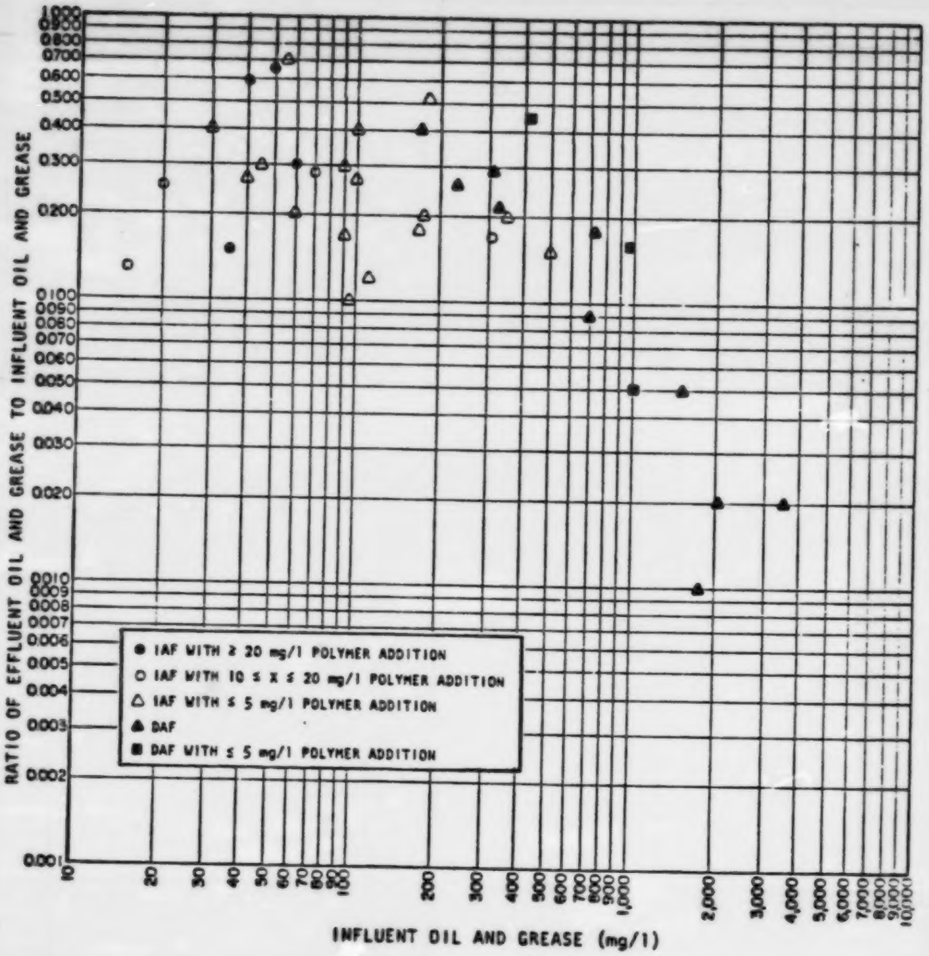

FIGURE 16. Air flotation efficiency as a function of influent oil and grease concentration.

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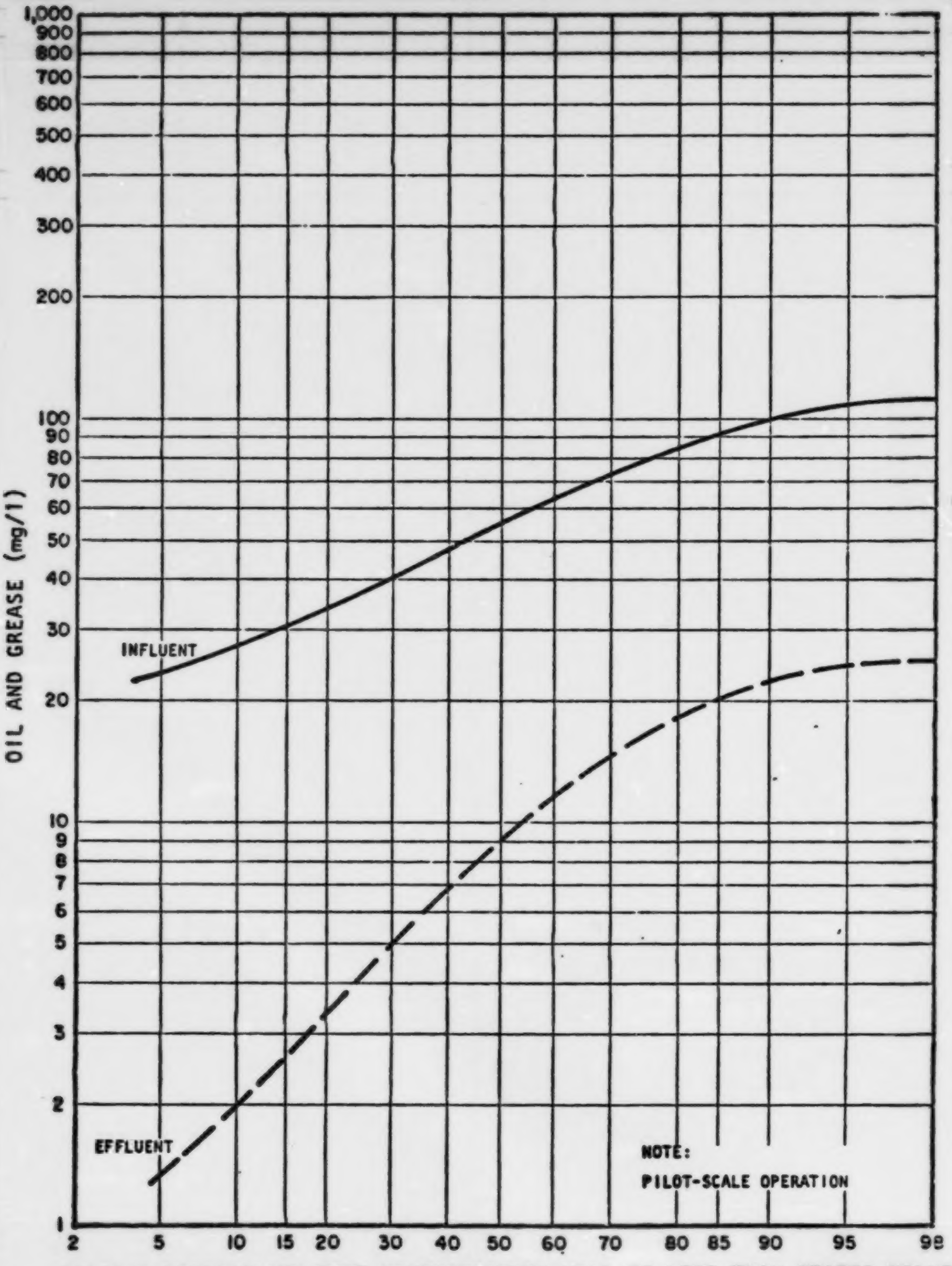

FIGURE 17. Variation in IAF treatment performance for oil and grease removal

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Operation data for an IAF unit treating petroleum refinery ballast wastewater are presented in Table 14. This pilot-scale unit was operated under closely controlled hydraulic conditions. In general, suspended solids removal was unimpressive, exhibiting a mean removal of 33 percent with greatly decreased efficiency at the higher influent solids concentrations. Conversely, effluent oil concentrations were consistently low with increased oil removal efficiency at the higher influent oil concentrations. In addition, the IAF unit produced a large volume of float material which was between four and nine percent of the throughput volume.

The variations in the treatment performance of both a TPS unit and an IAF unit used for suspended solids removal from petroleum refinery ballast wastewaters are presented in Figure 18. These data are depicted as a function of anticipated probability of occurrence. The curves presented in Figure 18 indicate that the overall removal of suspended solids by the aforementioned processes will increase with increased influent solids concentrations which also was observed with the removal of oil and grease.

Curves which depict the relative treatment performance of oil-water separators for the removal of dispersed and some emulsified oil fractions from refinery wastewaters are presented in Figure 19. As discussed in the preceding paragraphs, gravity differential oil-water separators of either the API or TPS type are needed to absorb shock oil loadings since excessive influent oil concentrations will reduce the performance of DAF and IAF oil removal systems. Of the two gravity separators, both perform reasonably well and are low energy and low maintenance systems. Although API separators are more widely used for primary oil removal, the current trend is to install TPS units because of their more economical price and reduced space requirements. The data presented in Figure 19 indicate that a TPS unit also will experience better oil removal efficiency than the conventional API separator. Since gravity oil separation by itself cannot be depended upon to meet the influent oil criteria of biological treatment systems, additional oil removal by a DAF or an IAF unit will be necessary. The data presented in Figure 19 also indicate that an IAF unit is less stable than a DAF unit and it will obtain slightly lower oil removal efficiencies, as illustrated.

Recently, pilot-scale fibrous-bed coalescers have been applied to wastewater treatment for the removal of residual secondary oil-water emulsions that are not separable under prolonger detention in gravity separators. A fibrous-bed coalescer is a fixed-filter element constructed of fiberglass or other materials which act to coalesce oil droplets and break emulsions. In a continuous water phase, oil droplets have a great affinity for the special fibrous materials (some fibers are less than 0.5 microns in diameter) contained in the coalescing element. When oil-water emulsions are forced through the element, the micronic oil droplets preferentially adhere to the fibers where coalescence takes place. As the oil droplets grow, they migrate through the elements. The droplets emerge from the coalescer elements large enough to rapidly rise to the surface of the water. The velocity of flow is controlled by the design of the separator to prevent oil droplets from being entrained with the flow of wastewater. The oil is removed from the water surface by skimmers or other withdrawal devices and the oil free water leaves the bottom of the separator.

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TABLE 14. EVALUATION OF INDUCED AIR FLOTATION TREATMENT PERFORMANCE*

Parameter	Influent		Effluent		Percent Removal Efficiency	
	Mean	Standard Deviation	Mean	Standard Deviation	Mean	Standard Deviation
Oil and Grease, mg/l	29	13	6	4	76	17
Suspended Solids, mg/l	70	40	45	38	33	37
BOD_5, mg/l	92	13	57	15	38	15
COD, mg/l	239	74	126	49	47	16
TOC, mg/l	115	18	77	13	33	10
Phenol, mg/l	9	6	6	5	32	29
Turbidity, standard units	122	27	63	26	47	24
Color, standard units	2	1	1	1	54	41

*Evaluation performed with a pilot-scale IAF unit on petroleum refinery ballast wastewater.

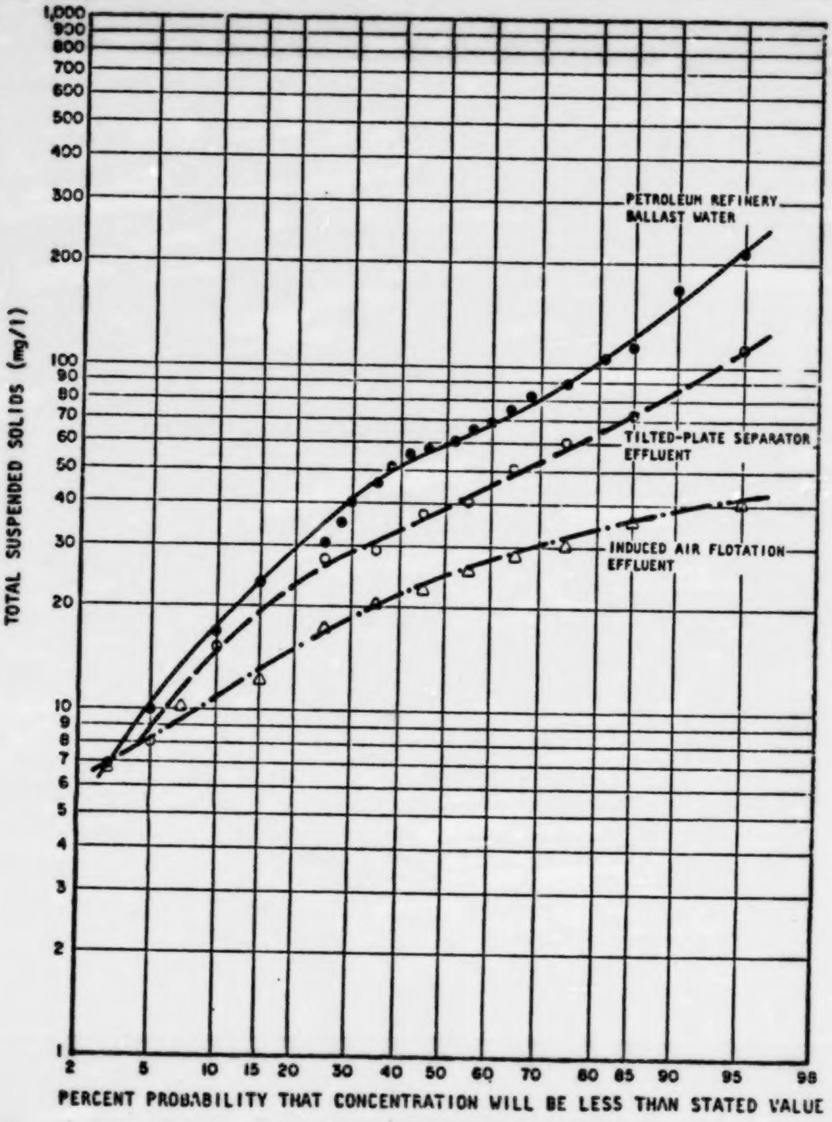

FIGURE 18. Variation in TPS and IAF treatment performance for suspended solids removal

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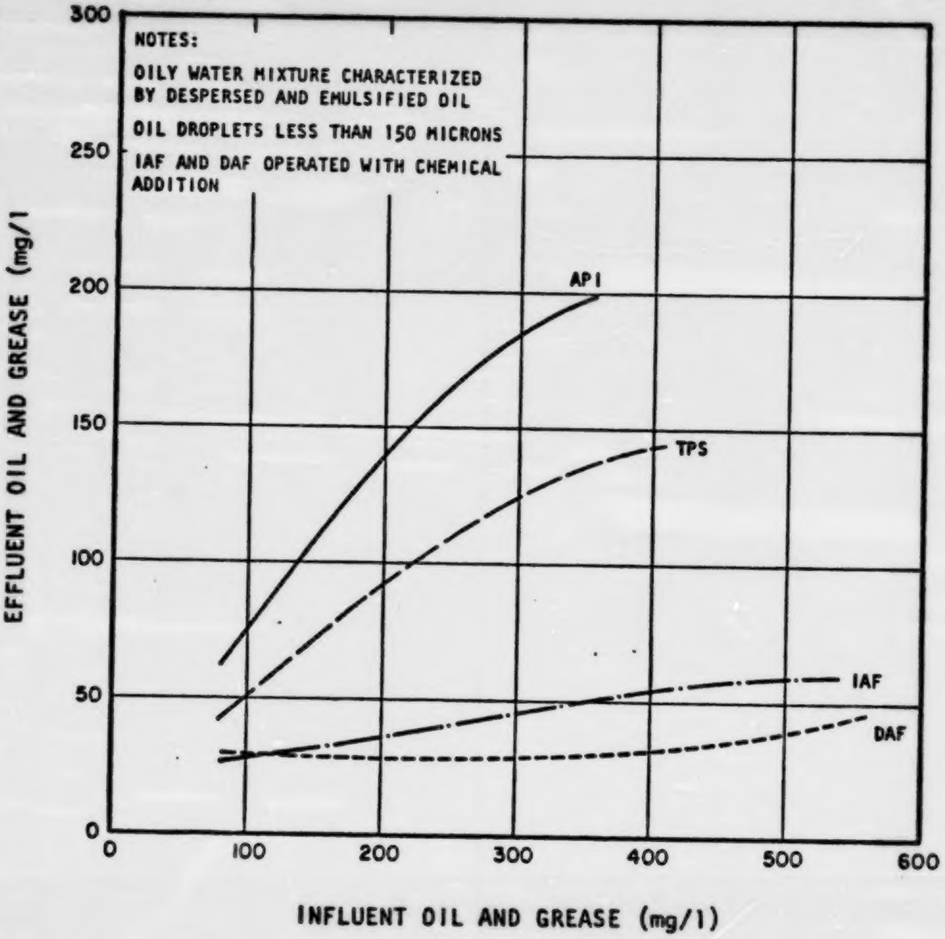

FIGURE 19. Relative performance of oil-water separators for treatment of dispersed and emulsified oils

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Coalescence in a fibrous bed involves three steps; namely: (1) interception of fine oil droplets by fibers; (2) attachment of droplets to the fibers or retained droplets; and (3) release of enlarged droplets from the fibers. The actual process of demulsification is due to the rupture of the interfacial film which surrounds each droplet when the emulsion flows through the small passages in the fibrous media. The subsequent coalescence of the dispersed oil phase is due to the preferential wetting characteristics of the media surface.

Experimental observations with laboratory-scale coalescers have shown that steady-state oil removal can be achieved after the fibrous beds are saturated with dispersed oil, and continuous operation is possible before excessive pressure drops are realized[193,194]. Data which illustrate the treatment performance of fibrous-bed coalescers for oil removal from oil and gas production effluents are presented in Figure 20. Included with this information are treatment performance data for oil removal from oil and gas production effluents using a DAF unit and a PPI separator[195]. These data indicate that at low levels of oil present in the wastewaters sampled, the DAF unit with chemical addition performed comparably with the fibrous-bed coalescer[195]. It should be emphasized that the efficiency of a fibrous-bed coalescer is dependent on such operating parameters as influent oil concentration, fiber size, flow rate, oil wettability, oil droplet sizes, and solids concentration.

Filtration systems have been applied to the separation of free and emulsified oil from refinery wastewaters. A broad spectrum of materials ranging from glass, porous ceramic, metals, plastics, sand, anthracite, to graphite have been tested as filter media. These media exhibit a specific affinity for oil. Filtration as a pretreatment step for oil and solids removal can be used independently or in conjunction with gravity separators or air flotation systems.

The oil removal mechanism is by direct filtration and induced coalescence where even small solid particles and oil globules are separated and retained on the media. This filtration and coalescing process is often enhanced by the use of polymer resin media.

Experimental observations with pilot-scale filtration coalescers have proven that the filtration process is effective for breaking emulsions[196,197]. The applications of a filtration process based on most experimental observations is best suited for selected solids-free streams where the media can serve as a coalescer and not as a collector of oil. This would greatly increase the run times associated with this oil removal process. Experimentation with pilot-scale membrane processes such as ultrafiltration or reverse osmosis has indicated that effective oil removal can be achieved, but at relatively low flux rates. Moreover, membrane fouling and membrane-life problems prevent the practical application of such processes for oil and grease removal from refinery wastewaters.

The primary advantages and disadvantages of such oil removal process applied to the treatment of refinery wastewaters discussed in previous sections of this report are presented in Table 15. A discussion regarding the oil removal potential of both biological

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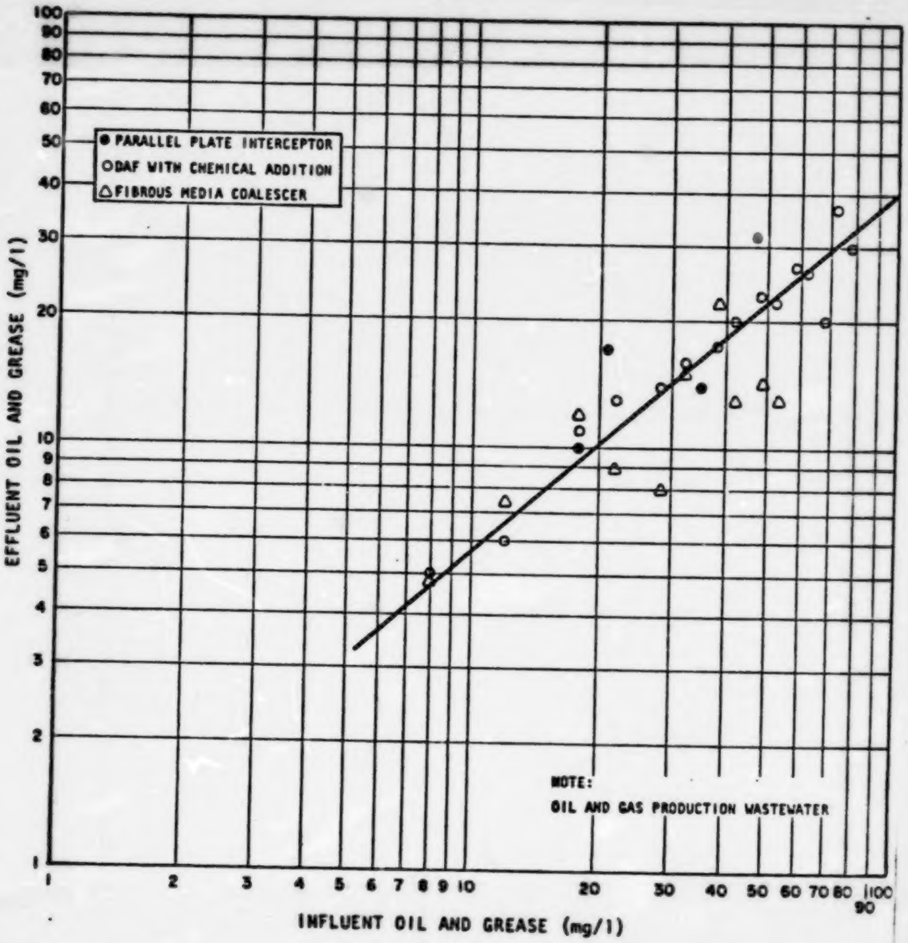

FIGURE 20. Relative oil-water separator performance when treating low levels of oil in wastewater.

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TABLE 15. PROCESS COMPARISON FOR OIL AND GREASE REMOVAL

Process	Description	Advantages	Disadvantages
Gravity Separation	API, CPI, TPS, PPI	Potential for treatment of suspended solids; effective removal of free and dispersed oil; simple and economical treatment operation.	Limited efficiency for removal of emulsified oil; will not remove soluble oil; restricted to the removal of oil droplets greater than 20 microns.
Air Flotation	DAF, IAF	Potential for treatment of suspended solids; effective removal of dispersed and emulsified oil with chemical addition; reliable process which effectively treats shock loads.	Chemical sludge handling when coagulants are used.
Chemical Flocculation	Used in conjunction with gravity separation and air flotation.	Potential for treatment of high suspended solids.	Chemical sludge produced.
Filtration	Sand, anthracite, multimedia, crushed graphite.	Effective suspended solids removal; has application to the separation of free, dispersed and emulsified oil.	Requires backwashing and the backwash creates a subsequent treatment problem.
Coalescence	Fibrous media	Effective removal of all oil components except soluble oils.	High levels of suspended solids will induce fouling; potential for biological fouling; needs extensive pretreatment; not demonstrated as a practical process in full-scale operation.
Membrane Process	Reverse osmosis	Soluble oil removal demonstrated in laboratory tests.	Low flux rates; membrane fouling and limited membrane life; not demonstrated as a practical process in full-scale operation; needs extensive pretreatment.
Biological Processes	Activated sludge, RBS	Effective soluble oil removal.	Requires extensive pretreatment to reduce influent oil levels to less than 40 mg/l.
Carbon Adsorption	GAC will act both as effective filtration medium and coalescing separator; PAC for removal of soluble oils only.	Effective removal of all oil components including soluble oils.	Requires extensive pretreatment; process is expensive; carbon must be regenerated or replaced; not demonstrated as a practical process for full-scale operation.

and carbon adsorption treatment processes will be presented in subsequent sections of this report.

Intermediate Treatment Processes

The need to equalize wastewater surges from refinery and petrochemical processing units as an intermediate step in a treatment system is well established. Biological processes as well as physical-chemical systems operate more efficiently if the pollutant concentration and flow of the wastewater are relatively constant. The objective of equalization is to minimize or control fluctuations in wastewater characteristics, thereby providing optimum conditions for subsequent treatment processes. The size and type of the required equalization basin will vary with the quantity of wastewater and the variability of the pollutant concentration. Many of the wastewater discharges within a refinery complex are from washdowns, tank cleanings, batch operations, and inadvertant spills. Adequate equalization would provide damping of the organic fluctuations associated with these intermittent wastewater sources in order to prevent shock loading of the biological treatment system.

Mixing is usually provided to ensure adequate pollutant concentration equalization and to prevent settleable solids from depositing in the basin. In general, the design problem consists of determining a functional relationship between the size of the equalization facility and the probable reduction in the fluctuations associated with the pollutant concentration of the wastewater. When flow varies considerably, and not in the same manner as the pollutant concentration; the equalization facilities should be physically arranged to provide additional storage beyond the normal required volume in order to dampen both the flow rate and concentration. Such off-specification impoundment of hydraulic surges and high organic loadings would require additional pumping capacity. The required size and mixing features of the equalization basin depend on the wastewater characteristics, process plant operating schedule, and any unusually severe operational fluctuations.

The presence of an equalization basin will often minimize the chemical requirements necessary for neutralization of wastewaters by mixing acidic and alkaline streams which would normally be discharged from the refinery at different times. Although refineries and petrochemical installations have many individual streams which are highly acid or alkaline, the combined wastewater discharge is generally slightly basic within a pH range between 7 and 10. Consequently, the combined wastewater from many installations does not require neutralization; however, the separate discharge of certain streams must be neutralized. Such streams include dilute acid or alkaline was waters, spent caustics from caustic treating operations, acid sludges from alkylation, acid treating processes, and spent acid catalysts.

Typical applications where neutralization is required include: (1) emulsion breaking through acidification and neutralization following gravity separation; (2) neutralization prior to biological treatment; (3) neutralization of specified streams to prevent corrosion; (4) pH adjustment to prevent unwanted precipitation of certain

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constituents; and (5) pH adjustment to enhance coagulation and sedimentation.

Design of a neutralization system is predicated on titration curves which determine the total alkalinity or acidity of a solution. These curves graphically depict the pH change per milliequivalent of reagent. The design and control of a neutralization process includes consideration for mixing, reagent feed, and pH control systems. The economics of the neutralization system depend on the characteristics and quantity of wastewater neutralized and the source and supply of neutralizing agents.

Biological Treatment Processes

The treatment of wastewaters discharged from refinery-petrochemical installations encompasses the removal of many pollutants, but most of the attention in refinery pollution control is focused on organic removal. Biological treatment is generally considered the most effective technique available for removing organic materials from petroleum refinery wastewaters. Essentially, the basic biological treatment processes include suspended growth activated solids systems, fixed microbial slime systems, and waste stabilization lagooning. Usually wastewater pretreatment is required to remove oils, suspended solids, and toxic substances. Additional unit operations required to maximize process stability are provided by such processes as neutralization, equalization, and surge or holding capacity (off-specification impoundment) as was previously discussed.

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The principal suspended growth activated solids system which is most effective in the treatment of refinery-petrochemical wastewaters is the activated sludge process. This is a continuous treatment system in which a microbial population is contacted with wastewater in a completely-mixed reactor and then separated by gravity from the treated liquor. The basis for the design of an activated sludge process is predicated on maintaining an environment in the bioreactor which is optimal for the growth and activity of select populations of acclimated microorganisms.

Treatability studies using bench- or pilot-scale process simulation techniques are used to formulate the basic design criteria for suspended growth systems and predict treated effluent quality. These treatability studies are conducted: (1) to vertify the applicability of biologically stabilizing the organic constituents in the wastewater; (2) to develop the basic kinetics for process design; (3) to establish the impact of various organic and inorganic wastewater constituents upon biological process efficiency; and (4) to predict the treated effluent quality and evaluate this quality in terms of effluent requirements. This process simulation will provide predictor relationships in the form of mathematical expressions which describe the activated sludge process and its applicability to the treatment of the given wastewater.

The actual degree of treatability characteristic of a refinery wastewater is a function of the type of refinery, the type of crude charge, the age of the facility, the type of collection system, the quantity of utility water blowdown, and the degree of inplant control. For these reasons, the actual design of the basic activated sludge process may vary from one installation to another.

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Petroleum refinery wastewaters, while highly variable in nature, tend to exhibit similar biological treatability characteristics. Consequently, if the wastewater characteristics for a given refinery are known and the capacity of the various refinery processes are considered, it is possible to use historical data collected during bench-scale treatability studies on other petroleum refinery wastewaters to obtain the required design coefficients. The pertinent design coefficients fit mathematical models which describe the biological oxidation process. These models depict the rate of substrate removal in a completely-mixed bioreactor, the growth of biological cells, and the oxygen requirements for oxidation of the organic material and cell synthesis.

For the completely-mixed activated sludge process, the soluble organic content of the treated effluent is equal to that in the bioreactor. Organic removal results from the physical enmeshment of suspended material in the biological floc, the flocculation and absorption of colloidal organics in the biological floc, and the biological oxidation of soluble organics which results in direct cell synthesis. The suspended and colloidal organics present in refinery wastewaters are essentially removed by the pretreatment processes for primary and secondary oil and solids separation. Therefore, the activated sludge process is primarily designed to achieve a reduction in the soluble organic content of refinery wastewaters.

The Kinetic model which describes soluble substrate removal in a completely-mixed bioreactor is:

$$[S_o - S_e]/[X_a t] = k S_e - y \qquad (1)$$

where S_o is the influent organic concentration; S_e is the effluent organic concentration; X_a is the average mixed liquor volatile suspended solids (MLVSS) under aeration; t is the detention time; k is the organic removal rate coefficient; and y is the nonremovable or refractory portion of the organic constituents[198].

The total oxygen requirement for maintenance of a biological treatment system is represented as follows:

$$R_r V = a' (S_o - S_e) Q + b' X_a V + I Q \qquad (2)$$

where R_r is the oxygen requirements; a' is the fraction of organics oxidized; b' is the oxygen required for endogenous respiration; Q is the flow; I is the immediate oxygen demand; and V is the volume of the aeration basin[198].

The sludge accumulation can be estimated as follows:

$$\Delta X = Q X_o + a(S_o - S_e) Q - [b X_a V + Q X_e] \qquad (3)$$

where a is the fraction of organics converted to cell mass; b is the fraction of sludge

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oxidized by endogenous respiration; X_o is the influent suspended solids; X_e is the effluent suspended solids; and ΔX is the net sludge accumulation[198]. The basic theory of biological wastewater treatment and the kinetic development behind each of the aforementioned models are adequately described elsewhere[198].

Engineering-Science, Inc. (ES) has conducted numerous investigations into the treatment of petroleum refinery wastewaters in which waste characterization and bench-scale activated sludge treatability data were collected. Table 16 summarizes the results of nine different investigations into the biological treatment of refinery wastewaters and lists the biological coefficients which characterize these wastes. The majority of these data are presented in terms of COD. In general, the organic removal rate coefficient in terms of COD varied from a low of 0.007 liters per milligram of VSS per day to a high of 0.017 liters per milligram of VSS per day at 24°C for the refinery wastewaters investigated. The highest value for the organic removal rate coefficient presented in Table 16 indicates the likelihood of extensive stripping of organics to the atmosphere during aeration of the wastewater. A typical magnitude of the organic removal rate coefficient characteristic of petroleum refinery wastewater treatment would probably be situated between 0.008 and 0.01 liters per milligram of VSS per day at 24°C.

With several exceptions, the majority of the sludge accumulation coefficients characteristic of refinery wastewaters varied between 0.4 and 0.5 for the magnitude of "a" and from 0.06 to 0.1 for "b". The range associated with the oxygen requirement coefficients a' and b' is 0.35 to 0.6 and 0.01 to 0.14, respectively.

The activated sludge process, by virtue of its high MLVSS concentration, is classified as a high-rate biological process which can tolerate more concentrated contaminant levels in its influent stream. In general, biotoxicity in an activated sludge process can be minimized or completely circumvented by in-plant controls, effective equalization, and complete mixing of aeration basins. Most plant upsets result from inadvertent dumps or spills into the process sewer which shock the biological system. The discharge of excessive levels of chromates, sulfides, ammonia, free oil, or other known biotoxicants common to refinery-petrochemical wastewaters also will severely upset biological treatment.

The major design considerations for the successful activated sludge treatment of refinery wastewaters include: (1) the organic loading; (2) the organic removal kinetics; (3) the organic and inorganic fluctuations of the wastewater; (4) the free oil loading; (5) the temperature effects; (6) the potential biotoxic or biostatic effects; (7) the oxygen utilization and sludge production rates; and (8) the settleability and thickening characteristics of the biological sludges. The design organic loading for most activated sludge systems will range from a low of 0.10 pounds of BOD_5 per pound of MLVSS per day for extended aeration to a high of 1.0 pounds of BOD_5 per pound of MLVSS per day. Higher loadings generally result in poorer treatment efficiency and higher treated effluent organic levels.

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TABLE 16. BIOLOGICAL TREATMENT COEFFICIENTS FOR PETROLEUM REFINERY WASTEWATERS

Case	EPA Category	Refinery Size (MBPD)	Organic Removal Rate* $\left(\frac{1}{\text{mg VSS - day}}\right)$		Sludge Growth Coefficients				Oxygen Requirement Coefficients				Average Residual COD (mg/l)
			BOD_5 Basis	COD Basis	BOD_5 Basis		COD Basis		BOD_5 Basis		COD Basis		
					a	b	a	b	a'	b'	a'	b'	
1	E	406	0.017	0.0068	-	-	-	-	-	-	0.57	0.10	106
2	C	60	-	0.0086	-	-	0.50	0.06	-	-	0.60	0.11	53
3	D	90	-	0.0077	-	-	0.50	0.06	-	-	0.36	0.07	100
4	C	63	-	0.0044	0.50	0.08	0.44	0.10	-	-	0.35	0.083	140
5**	E	427	-	0.010	-	-	0.26	0.03	-	-	0.46	0.05	100***
6	E	427	0.0035	-	0.50	0.05	-	-	0.47	0.28	-	-	-
7	B	205	0.017	0.0165	-	-	0.20	0.08	-	-	0.40	0.01	76
8	C	88	-	0.010	-	-	0.43	0.10	-	-	0.52	0.14	82
9	B	92	0.006	-	0.52	0.03	-	-	0.53	0.17	-	-	-

*Approximate temperature 24°C.

**Pilot-scale biological reactor.

***TOD

A low-rate suspended growth activated solids system in which oxygenation and mixing are normally provided by mechanical surface aerators is the aerated lagoon biological treatment process. The mechanical aeration system is designed such that the power levels are normally too low to maintain dissolved oxygen in all portions of the basin or to completely mix the system. The operating MLVSS level is normally between 2 and 10 percent of that maintained in an activated sludge process; consequently, aerated lagoons are more sensitive to transient organic loadings, toxic substances, and temperature effects.

Aerated lagoons are operated at high organic loading levels because of the low concentration of microorganisms suspended in the wastewater. These loadings usually vary between 1.0 and 2.0 pounds of BOD_5 per pound of MLSS per day. The aerated lagoon is effective for the treatment of most hydrocarbons such as those present in the discharge from topping plants, but exhibits a reduced efficiency for the treatment of more complex wastewaters such as those discharged from integrated refineries[189].

Because of the low mixing levels in aerated lagoons, large volumes of oily solids tend to settle within the basin where they decompose anaerobically releasing additional BOD to the upper layers of the lagoon. This feedback can be as high as 20 percent of the influent organic load during the summer months. Moreover, winds tend to stir up bottom sediments, causing a deterioration of effluent quality in terms of suspended solids and partially stabilized oily material.

A tabulation of effluent-quality data from a modified aerated lagoon treating petroleum refinery wastewaters is presented in Table 17. This aerated lagoon was operated with intermittent solids recycle and post-clarification of the effluent, thus providing a greater degree of operational control. These data indicate a better effluent quality than normally associated with aerated lagoon treatment. The conventional approach to aerated lagoon design specifies that the treatment unit will function either as a process preceding waste stabilization lagooning or as an interim treatment process which can be converted to an activated sludge system as was the case illustrated by the data presented in Table 17.

Temperature is a particularly important variable in the biological treatment of refinery wastewaters, and the influence of temperature on biochemical reactions is well-documented[189]. Excessive temperature losses through a biological treatment system during winter months in a northern climate might lower microbial activity to the point of failing to meet effluent BOD quality standards. In general, temperature effects are more pronounced with the increasing solubility and complexity of the wastewater and activated sludge treatment would be significantly affected by aeration basin temperature.

The level of oil and grease discharged to a biological treatment system can have a significant impact on treatment performance. In general, hexane extractable oils will adversely affect a biological system as the concentration of free and emulsified oils in the mixed liquor approaches 50 to 75 mg/ℓ. The most significant problem associated with the presence of oil in biological systems is attributed to the lowering of floc density to a

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TABLE 17. EFFLUENT QUALITY FROM A MODIFIED AERATED LAGOON TREATING PETROLEUM REFINERY WASTEWATERS* (MONTHLY AVERAGE DATA)

	Parameter						
Month	Suspended Solids (mg/1)	COD (mg/1)	BOD_5 (mg/1)	NH_3-N (mg/1)	Phenols (mg/1)	Total Cyanide (mg/1)	Oil and Grease (mg/1)
January	28	221	52	20	0.024	0.119	8.3
February	28	196	22	41	0.114	0.167	3.3
March	30	122	23	38	0.044	0.40	2.8
April	25	99	15	45	0.028	0.052	2.6
May	21	88	9	36	0.024	0.076	2.0
June	26	81	10	28	0.036	0.041	1.7
July	24	90	14	22	0.031	0.04	1.5
August	33	90	12	37	0.024	0.09	1.9
September	22	72	11	30	0.017	0.045	1.0
October	17	108	15	29	0.024	0.045	1.8
November	27	131	27	48	0.011	0.22	2.7
December	23	110	18	32	0.015	0.17	3.5

*EPA Category D.

level where the sludge settling properties are destroyed. Free oils will coat the biological floc and prohibit the efficient transfer of oxygen and substrate within the biomass. The apparent quantities of oil associated with the loss of suspended solids from a secondary clarifier are indicated graphically in Figure 21. The accumulation of oil on sludge particles will contribute to effluent quality deterioration. Therefore, pretreatment facilities for oil-water separation should be capable of removing oil to an acceptable concentration level for efficient operation of the biological treatment process.

Biological treatment processes are very limited in their potential for oil removal. While microorganisms are capable of oxidizing most soluble oil fractions present in refinery wastewaters, they are limited in their ability to degrade free and emulsified oils within the contact times characteristic of most biological treatment processes. The best documentation of biological process effectiveness for the removal of oil is the analysis of full-scale plant operation. ES has compiled effluent oil quality data from selected biological treatment plants handling refinery wastewaters. These data are presented in Figure 22 as a function of anticipated probability of occurrence. These case histories present operational data for an activated sludge process operated both with and without polymer addition to the secondary clarifier, an activated sludge process with tertiary filtration, an aerated lagoon process, and an aerated lagoon process with tertiary filtration. Although these data were obtained for treatment of wastewaters from refineries which represent various production subcategories (as defined by EPA), refine crudes of varying characteristics, and have other process idiosyncrasies which impact on the raw wastewater characteristics; they do indicate a probable range of obtainable effluent oil and grease levels. The median values range from a low of 3.0 mg/ℓ to a high of 12 mg/ℓ effluent oil and grease, while two percent of the observed values (98 percentile probability) exhibited a range from 20 to 60 mg/ℓ effluent oil and grease concentrations. With the addition of tertiary filtration, biological treatment processes can meet allowable Best Practicable Control Technology Currently Available (BPCTCA) discharge levels for the presence of oil and grease in treated refinery effluents[190,199].

The second type of biological treatment process to be considered herein is the fixed microbial slime system. In this system, attached microorganisms remove suspended and dissolved organic material from the wastewater as it flows over fixed slime surfaces. At the same time, oxygen is absorbed into the wastewater from the air which is induced through the system by natural draft. At the surface of the slime, oxygen and organics are made readily available to the microorganisms by mixing and diffusion in the wastewater. The effective film depth is that which is in immediate contact with the wastewater. The area between the filter media and the effective film depth is considered anaerobic because all oxygen is consumed before it can diffuse to the inner layer. The relative sizes of these two regions depend on the concentration of oxygen in the wastewater and the turbulence between the liquid film and the attached slime surface.

A typical fixed microbial slime system is the conventional trickling filter in which granular media are generally used to support the biological mass. The introduction of synthetic filter media, with low bulk density, has resulted in the use of deeper filters operated at greatly increased organic and hydraulic loading rates. Trickling filters are

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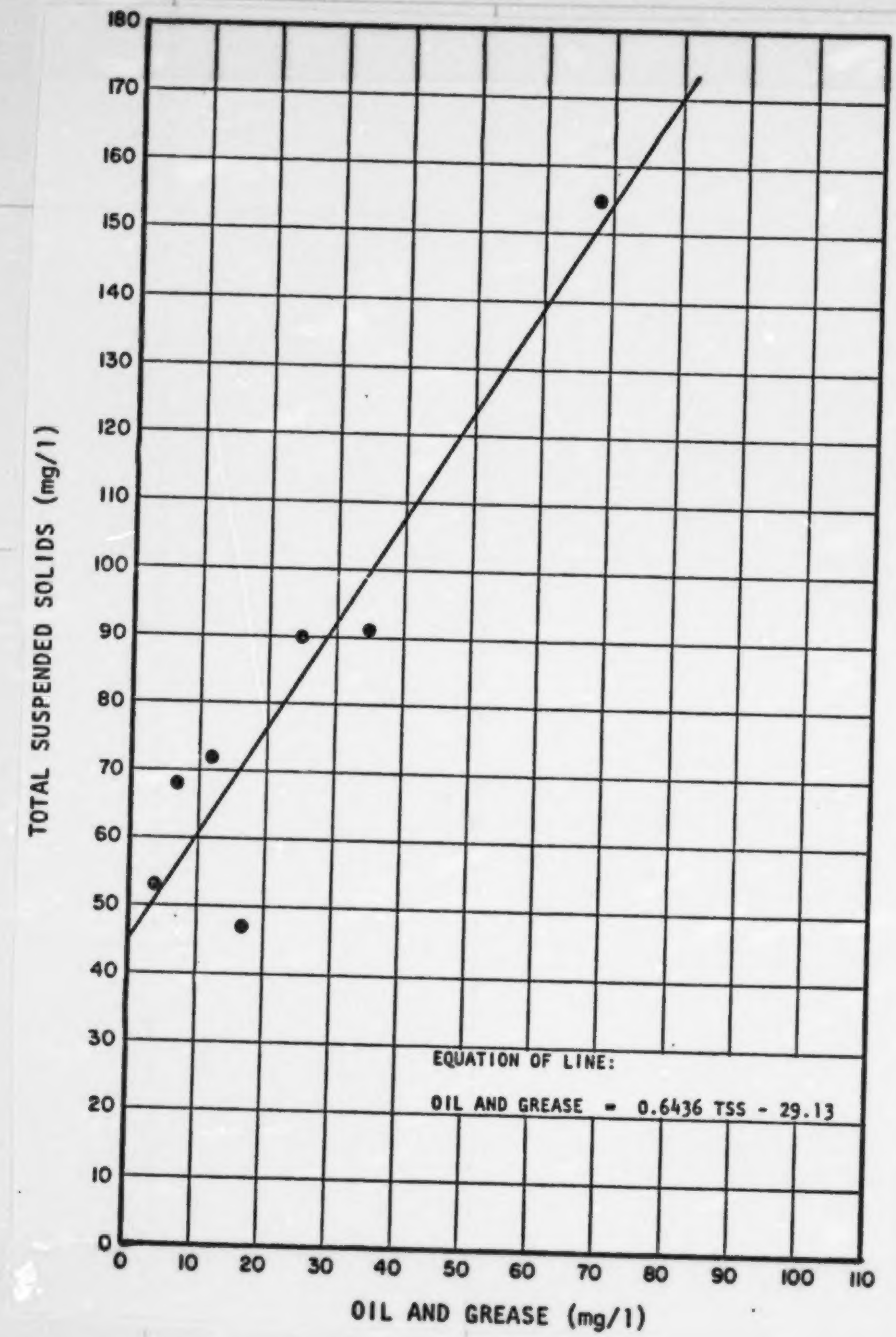

FIGURE 21. Relationship between suspended solids and oil and grease concentrations in biological treatment plant effluent

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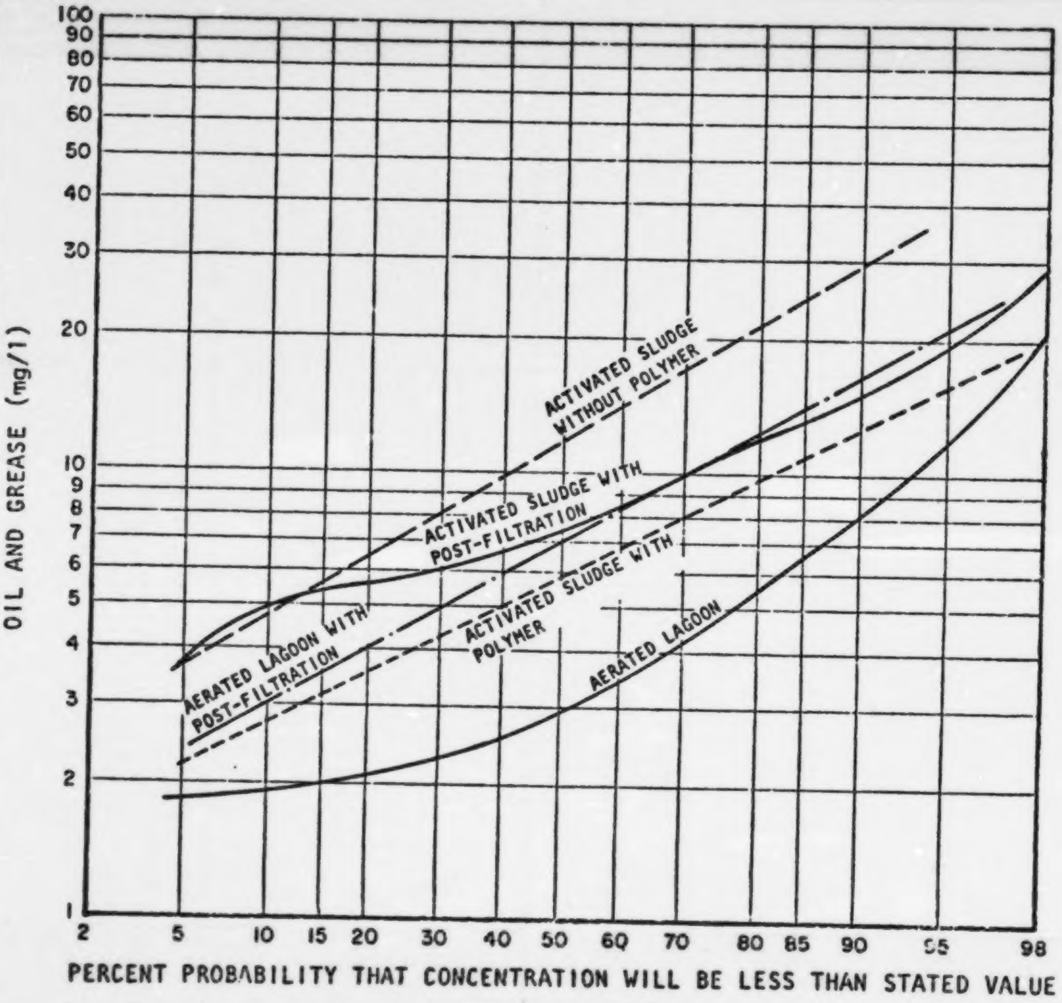

FIGURE 22. Effluent oil and grease from biological unit processes for the treatment of refinery wastewaters

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not used extensively for the treatment of refinery-petrochemical wastewaters since the trend is toward high-rate biological processes. Nevertheless, they do have application as roughing devices preceding other biological or physical-chemical units.

The rotating biological surface (RBS) unit is a fixed microbial slime system which has application as a secondary wastewater treatment system for handling refinery wastewaters. It consists of large-diameter plastic media mounted on a rotating horizontal shaft such that approximately 40 percent of the surface area comes in contact with the wastewater at any one time. The large microbial population which is fixed to the rotating surface permits a high degree of treatment in a short retention period. During rotation, the contactor carries a film of wastewater into the air which absorbs oxygen while trickling down the biological surface. Microorganisms in the biomass then remove both the dissolved oxygen and organic material from the wastewater. Further treatment occurs as the biological surfaces continue rotation through the bulk of the wastewater. The shearing forces exerted on the biomass as it passes through the wastewater cause excess slime to slough from the surface of the media. This prevents clogging of the media surfaces and maintains a constant microorganism population on the media. The turbulence induced by the rotation of the biological surfaces through the wastewater will maintain sloughed solids in suspension until the flow of treated wastewater is passed to secondary clarifiers for solids separation and disposal.

The biomass associated with the RBS unit is shaggy in appearance with many elongated macroscopic filaments which project outward into the adjacent liquid film of the wastewater. This provides a much larger active biological surface area than that defined by the surface area of the support medium. It also permits substrate and dissolved oxygen to reach a greater portion of the biomass. The nature of the attached biological growth is due primarily to the continual drag induced by contactor rotation through the wastewater and the draining of entrained liquor from the contactor surface.

The results of a pilot-scale study into the application of the RBS unit for the treatment of petroleum refinery wastewaters are presented in Table 18. In general, the effluent quality from this pilot-scale RBS unit compares favorably with other biological treatment processes. These data indicate that the effluent quality associated with an RBS unit is a function of hydraulic loading. For instance, better removals of soluble organics, oil and grease, and sulfides were obtained at the lower hydraulic loadings. On the other hand, a degree of stable nitrification was achieved at each of the hydraulic loadings examined during the study. Air stripping of ammonia was not considered responsible for the apparent reductions observed during the study because of the operating pH and temperature levels. Tests conducted in microorganism-free reactors indicated that the loss of less than 10 percent of the ammonia may be attributed to air stripping[200]. Since the apparent ammonia reductions experienced with the RBS unit were greater than 25 percent, a degree of nitrification did occur.

The variation in pilot-scale RBS treatment performance for both COD and oil removal is presented in Figure 23. In general, the RBS unit did not perform consistently well for the treatment of oil and grease indicating the need for tertiary treatment

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TABLE 18. PILOT-SCALE RBS EFFLUENT QUALITY FOR TREATMENT OF PETROLEUM REFINERY WASTEWATERS*

	COD	BOD_5	TSS	Oil and Grease	NH_3-N	Sulfide	Phenols
0.9 gpd/ft^2							
Mean (mg/l)	170	19	20	18	48	0.2	0.04
Standard Deviation (mg/l)	142	7	18	10	25	0.2	0.02
95 Percentile (mg/l)	448	33	55	38	97	0.6	0.08
Removal Efficiency Percent	58	90	-	65	26	99	79
1.9 gpd/ft^2							
Mean (mg/l)	156	25	28	12	48	0.3	0.03
Standard Deviation (mg/l)	70	6	11	11	18	0.1	0.01
95 Percentile (mg/l)	293	36	50	34	83	0.5	0.05
Removal Efficiency Percent	44	87	-	72	-	99	84
2.6 gpd/ft^2							
Mean (mg/l)	212	33	65	37	4	0.7	0.03
Standard Deviation (mg/l)	71	21	48	18	6	0.7	0.01
95 Percentile (mg/l)	351	74	159	73	15	2.1	0.05
Removal Efficiency Percent	35	69	-	66	32	88	77

*EPA Category D Refinery.

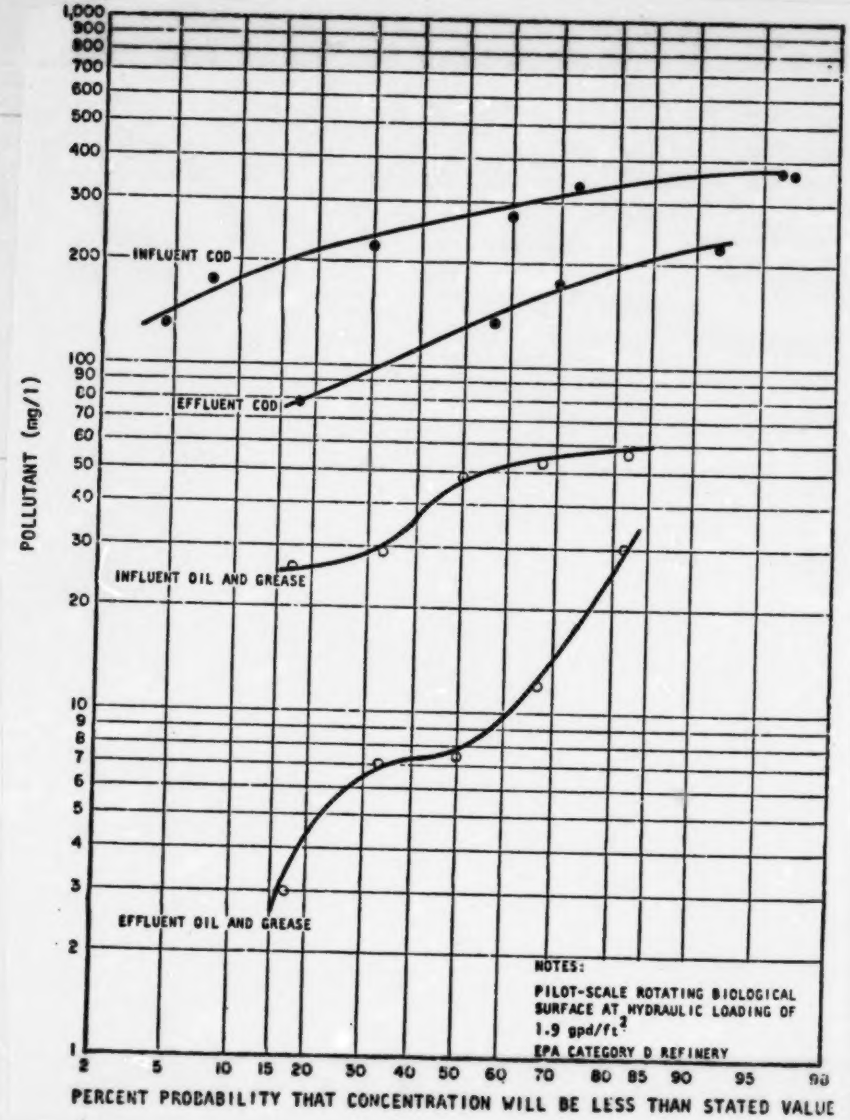

FIGURE 23. Variation in RBS treatment performance for COD and oil and grease removal

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processes to enhance effluent quality. The variation in pilot-scale RBS treatment performance for phenol removal is presented in Figure 24. The median effluent phenol concentration is approximately 0.025 mg/ℓ.

The third alternative biological treatment process for refinery wastewater treatment is that of waste stabilization lagooning. In general, waste stabilization ponds depend on the natural aquatic processes of bacterial and algal symbiosis which require sunlight as a primary energy source. Traditionally, waste stabilization ponds were used to provide long-term polishing of effluents discharged from upstream biological processes; although, they do have application as a total treatment system[189].

Since waste stabilization ponds are susceptible to wind action and short-circuiting, practical design application specifies a series of small ponds which provide more predicable performance. High organic loadings usually induce anaerobic conditions in the first pond. Moreover, the accumulation of oils in the waste stabilization pond prevents the penetration of sunlight, thereby restricting algal growth which also will induce anaerobic conditions.

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Waste stabilization ponds are not widely used in the United States for treatment of refinery wastewaters since this treatment process requires large amounts of land which may not always be available. This process is very temperature dependent and practical application must be restricted to warmer climates. Algal proliferation will often add to the effluent suspended solids level and cause effluent limitation violations even though the soluble organic fraction may be acceptable.

Tertiary Treatment Processes

Wastewater treatment technology which is designed to remove pollutants which are not adequately removed by conventional secondary treatment is defined as an advanced or tertiary treatment process. These pollutants may include soluble inorganic compounds such as ammonia, a soluble organic material which contributes BOD, suspended and colloidal solids, and bacteria. Two wastewater treatment processes which are most often applied as tertiary treatment are filtration and carbon adsorption.

In general, filtration has application as a treated effluent polishing process for treatment of effluent contaminated with suspended and colloidal material discharged from activated sludge treatment. Filtration removes most of these constituents and is usually required prior to carbon adsorption treatment.

The design and operation of a filtration process must consider such factors as (1) the mode of throughput; (2) the type of filtration media; (3) the distribution of media; (4) the underdrain system; and (5) the type of backwashing operation. Gravity filters operated in either the downflow or upflow mode are generally used for effluent polishing. In concept, all filters operate as three-dimensional strainers. Dual-media and multimedia filters act as multilayer strainers removing larger flocculated particles in the coarser media and smaller particles in the fine media. A filtration cycle terminates when the

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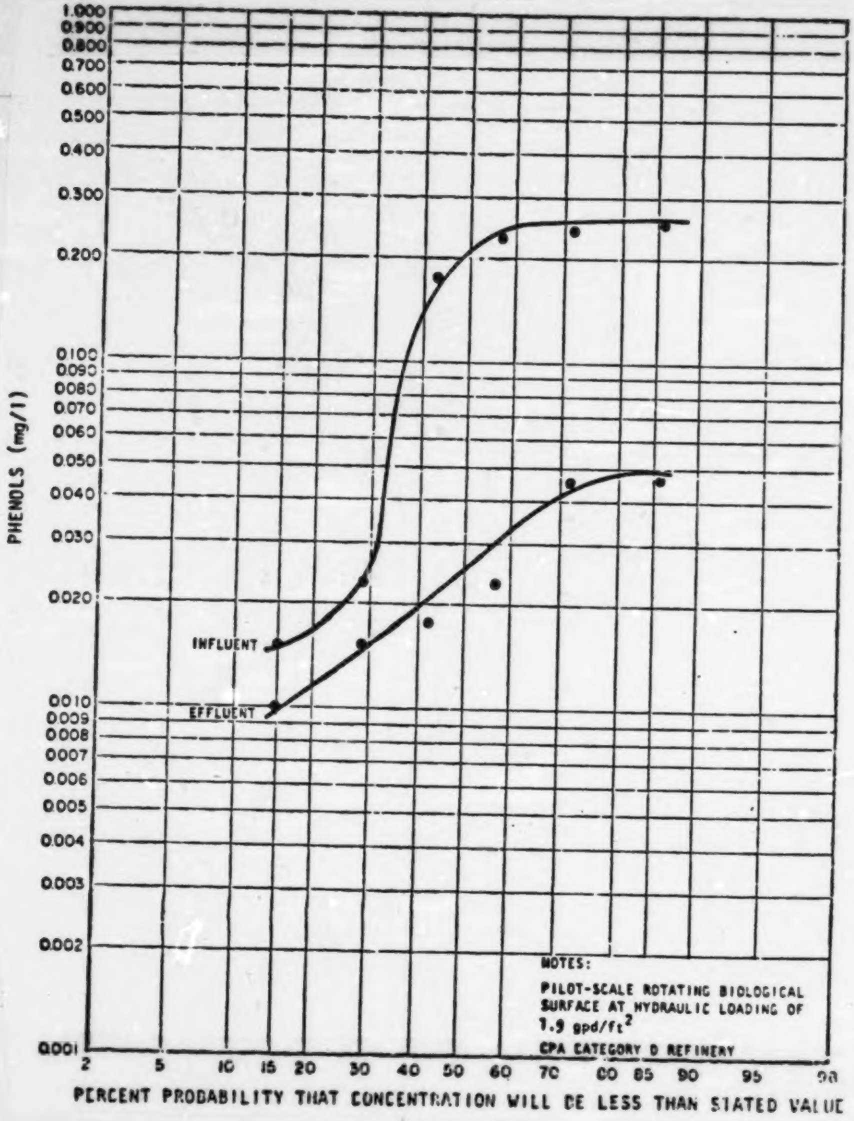

FIGURE 24. Variation in RBS treatment performance for phenol removal.

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amount of particulate matter escaping the filter exceeds the effluent guidelines or when the headloss through the filter caused by solids capture exceeds the limiting value.

A comparison of both the upflow and downflow mode of filter operation as applied to the tertiary treatment of petroleum refinery wastewaters is presented in Table 19. Both of these pilot-scale filtration units were fed biologically treated secondary effluents, chemically conditioned before application to the filter. Run times were considerably longer with the upflow sand filtration unit and the overall operational performance characteristics were more favorable.

Irrespective of their relative efficiency, all filters require the periodic removal of deposited material. Cleaning of a filter at the end of a run cycle is generally accomplished by high-velocity backwashing and the overall efficiency of a filtration unit is greatly affected by the amount of backwash water required. In general, the contaminated backwash water can be treated separately or rechanneled back through the biological process.

A measurement of filter efficiency is specific capture which represents the mass of particulate matter retained in the filter per square foot of surface area and foot of headloss. Specific capture is affected by approach velocity and loading rate since filters operating at higher loading rates will experience higher intergranular velocities, thereby driving solid particles deeper into the filter bed and increasing specific deposit. A number of values for specific capture determined from the operation of both shallow and deep-bed filtration units are presented in Table 20. In general, an increase in the magnitude of the specific capture or efficiency of the filter is offset by increased operational difficulties and maintenance problems.

General characteristics common to most filtration processes used for the treatment of biologically treated secondary effluents are: (1) that the variation in wastewater flow and effluent quality from biological treatment will not adversely affect filter efficiency; (2) that BPCTCA discharge limitations for suspended solids can be met with either deep-bed or shallow-bed filtration units; and (3) that filter performance is extremely sensitive to changes in media size and configuration.

A second tertiary treatment process applied to the removal of refractory trace organics from petroleum refinery wastewaters is carbon adsorption. Activated carbon adsorption involves the use of high surface area activated carbon as a physical media for surface adsorption of organic contaminants from wastewaters. The controlling design parameters are: (1) contaminant concentration in the waste stream; (2) temperature; (3) adsorbent area per unit volume; (4) adsorption characteristics of the contaminants; and (5) diffusion considerations. The principal advantages of activated carbon treatment include: (1) the ability to remove select organic molecules; (2) the ability to withstand shock loadings; (3) the ability to remove extremely low concentrations of sorbable contaminants; and (4) the relative ease of operation. Carbon adsorption is a valuable treatment process for the removal of potentially toxic organic materials. Its disadvantages include: (1) a high capital and operation cost; (2) fouling; (3) the inability to remove

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TABLE 19. COMPARISON OF UPFLOW SAND AND DEEP-BED TERTIARY FILTRATION FACILITIES FOR THE TREATMENT OF REFINERY WASTEWATERS*

Parameter	Upflow Sand	Deep Bed PVC Media
Hydraulic Loading (gpm/ft^2)	4 - 10	6 - 15
Cumulative Loading at Breakthrough (gal/ft^2)	1,800 - 4,000	200 - 850
Solids Loading at Breakthrough (lb dry solids/ft^2)	0.10 - 0.28	0.05 - 0.20
Pressure Drop at Breakthrough (psi/ft of bed)	0.35 - 0.90	2.5 - 8.0
Average Effluent TSS (mg/l)	5	16
Average Effluent BOD$_5$ (mg/l)	3	5
Average Effluent COD (mg/l)	73	74
Shape of Breakthrough Curve	Sharp Breakthrough	Continuous Deterioration of Effluent Quality
Effect of Chemical Addition	Alum and polyelectrolyte addition did not significantly effect solids loading, but did increase the pressure drop.	Alum and polyelectrolyte addition increased the solids loading.

*Pilot-scale study for EPA Category B Refinery.

TABLE 20. DESIGN CHARACTERISTICS FOR TERTIARY FILTRATION FACILITIES

Filter*	Media Type and Configuration	Hydraulic Loading (gpm/ft^2)	Specific Capture (lb dry solids/ft^2 per ft H_2O)	Effluent TSS (mg/l)
Deep Bed	24" sand and 36" anthrafilt**	7	0.015	4
Shallow Bed	16" sand***	2	0.010	10
Shallow Bed	16" sand†	2	0.046	2
Shallow Bed	16" sand††	2	0.022	4
Deep Bed	24" sand and 36" anthrafilt†††	3.5	0.07	2

*Pilot-scale study for EPA Category C Refinery.

**0.5 to 1.0 mm sand below 1.0 mm anthrafilt.

***0.5 to 1.0 mm sand above 1.2 mm sand.

†0.6 to 0.65 mm sand above 1.2 mm sand.

††0.6 to 0.65 mm sand above 1.0 mm sand.

†††0.5 to 1.0 mm sand below #3 anthrafilt.

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many inorganic compounds and some organic compounds; and (4) the necessity for extensive carbon regeneration equipment.

The two types of carbon adsorption technology applied to the treatment of refinery wastewaters are: (1) GAC in a continuous flow-through system and (2) the addition of PAC to an activated sludge process. Various approaches to the application of the GAC adsorption process are: (1) carbon-biological series treatment; (2) biological-carbon series treatment; and (3) carbon adsorption as a total process. Each of these applications requires primary treatment for the removal of oil and suspended solids.

Of the three GAC process applications indicated, only the series biological-carbon treatment scheme will probably be prevalent in the immediate future since many refineries already have made the capital investment in secondary biological treatment. The carbon-biological series treatment option has some apparent advantages in that it allows for a more effective use of carbon, dampens organic surges to the bioreactor, prevents biological upset by removal of biotoxic substances, and allows for a reduction in excess sludge production. Nevertheless, many of these advantages also are characteristic of the PAC adsorption process. Some obvious disadvantages are: (1) a potential effluent suspended solids and color problem associated with biological treatment; (2) a less efficient utilization of the biological process; and (3) a strong dependence on a sensitive biological process to consistently produce an effluent which will meet stringent quality requirements.

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The results of a pilot-scale GAC process treating the effluent from a conventional API separator are presented in Figure 25 in terms of a probability analysis. As illustrated in Figure 25, the effluent TOC concentration from the pilot carbon columns was consistently less than 30 mg/ℓ, although the influent TOC levels also were fairly low due to dilution with cooling water. The probability distribution of long-term mean effluent COD values from pilot-scale and full-scale GAC treatment systems treating refinery or related wastewaters is presented in Figure 26[199]. These data indicate that the effluent concentrations and removal capabilities of activated carbon vary significantly and must be assessed on a case-by-case basis. In general, a total carbon treatment system is not satisfactory because of excessive organic leakage to the effluent, and it should not be considered a process panacea for producing high-quality effluents[201].

The application of full-scale GAC treatment to a relatively low-strength refinery wastewater consisting primarily of contaminated storm water indicated mixed results in terms of both removal of organic materials and cost effectiveness. The operation of full-scale carbon facilities has indicated that carbon capacity, in terms of pounds of organics removed per pound of carbon applied, has generally been less than that determined during pilot-scale studies[202]. This can be attributed to the difference in adsorptive capacity between virgin carbon which is often used in pilot studies and regenerated carbon which is recycled in full-scale systems.

The PAC process may have wider application for the treatment of refinery wastewaters since it has been shown to improve the performance of biological treatment systems

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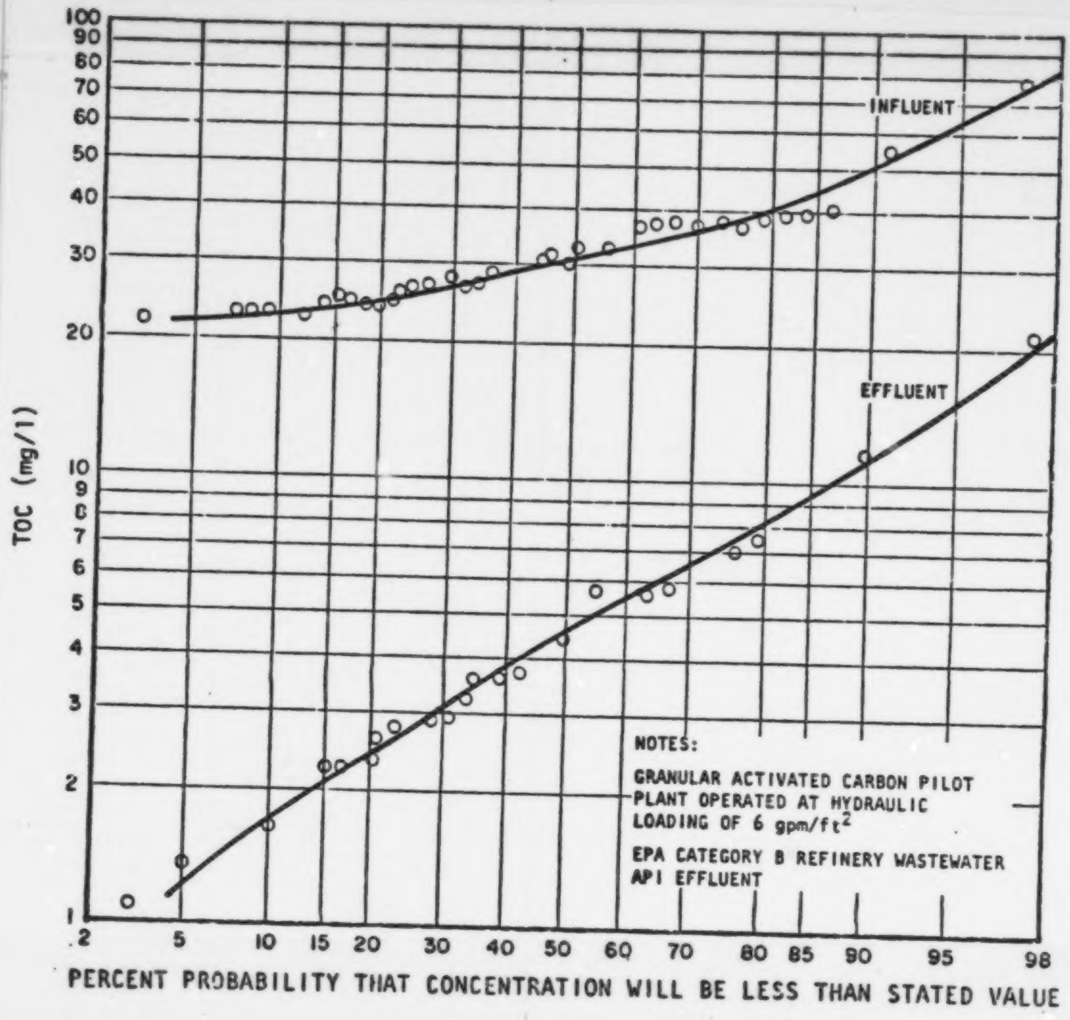

NOTES:

GRANULAR ACTIVATED CARBON PILOT PLANT OPERATED AT HYDRAULIC LOADING OF 6 gpm/ft^2

EPA CATEGORY B REFINERY WASTEWATER API EFFLUENT

FIGURE 25. Variation in GAC treatment performance for TOC removal

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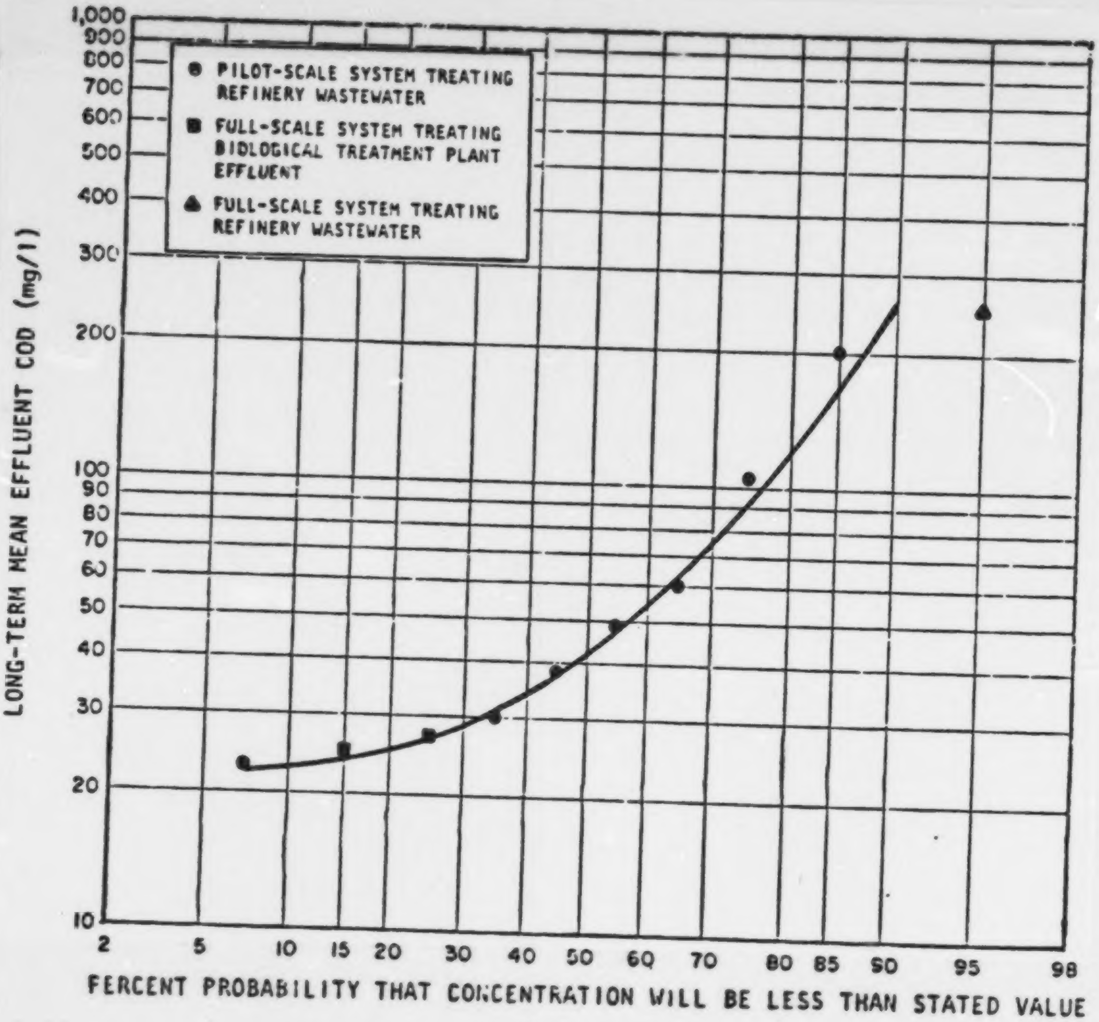

FIGURE 26. Effluent COD attainable from activated carbon system

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with a relatively minor addition of equipment to an existing plant. The primary operating parameter that defines the performance of a PAC process is the equilibrium carbon concentration in the aeration basin. This equilibrium carbon concentration is a function of the carbon dosage to the wastewater, the amount of carbon leaving in the final effluent, the quantity of carbon/biological sludge wasted, and the hydraulic retention time. It is estimated that a PAC variation of the activated sludge process can achieve an additional 54 percent TOC removal over conventional activated sludge treatment when treating refinery wastewaters[202]. In general, the performance of a PAC process is highly dependent on the type of carbon used.

GAC treatment has application both as a tertiary process for the removal of soluble oils from secondary treatment effluents and as a coalescing media for the separation of dispersed and emulsified oils. The oil and grease removal performance of a pilot-scale GAC system treating the effluents from a conventional API separator is presented in Figure 27. These data are illustrated in terms of the probability of occurrence and indicate that the median effluent oil and grease concentration was approximately 2.5 mg/ℓ. The variation in pilot-scale GAC treatment performance for oil and grease removal from aerated lagoon effluents is illustrated by the probability distributions presented in Figure 28. These data indicate the characteristic GAC treatment potential for the removal of soluble oils. The data presented in Figure 28 also indicate that the median effluent oil and grease concentration was less than 0.5 mg/ℓ. Both systems were preceded by sand filtration. In general, the aforementioned pilot-scale performance characteristics agree with other experimental observations[196]. Nevertheless, current operating experience with full-scale GAC treatment systems has indicated median oil and grease concentrations in the neighborhood of 8 mg/ℓ[203]. Two documented full-scale case histories indicating effluent oil and grease quality from GAC treatment of API separator effluents are presented in Figure 29. Although these data fall within the same range as oil and grease effluent qualities from the activated sludge and aerated lagoon processes, they do indicate that application of carbon adsorption treatment to refinery wastewaters is most effective as an organic removal step following biological treatment and sand filtration rather than as a replacement process for biological treatment.

SOLID WASTE DISPOSAL

Any attempt to improve the quality of a wastewater is generally accompanied by a solid waste disposal problem. Solid waste handling can be extremely costly, particularly in the case of wastewater sludges that must be dewatered prior to economical ultimate disposal. Because of the associated costs and increasingly stringent regulatory controls, solids handling and disposal operations must be considered an integral part of any treatment program in order for engineering or economic evaluations to be relevant.

The types of sludges generated by the petroleum refining industry are: (1) once-through cooling sludge; (2) cooling tower sludge; (3) alkylation sludge; (4) waste catalytic cracking catalyst; (5) spent treating clays; (6) tank bottoms; (7) storm water silt; (8) oil-water separator bottoms; (9) air flotation float; and (10) waste biological sludge. The general characteristics of these waste solids were discussed in previous sections of this

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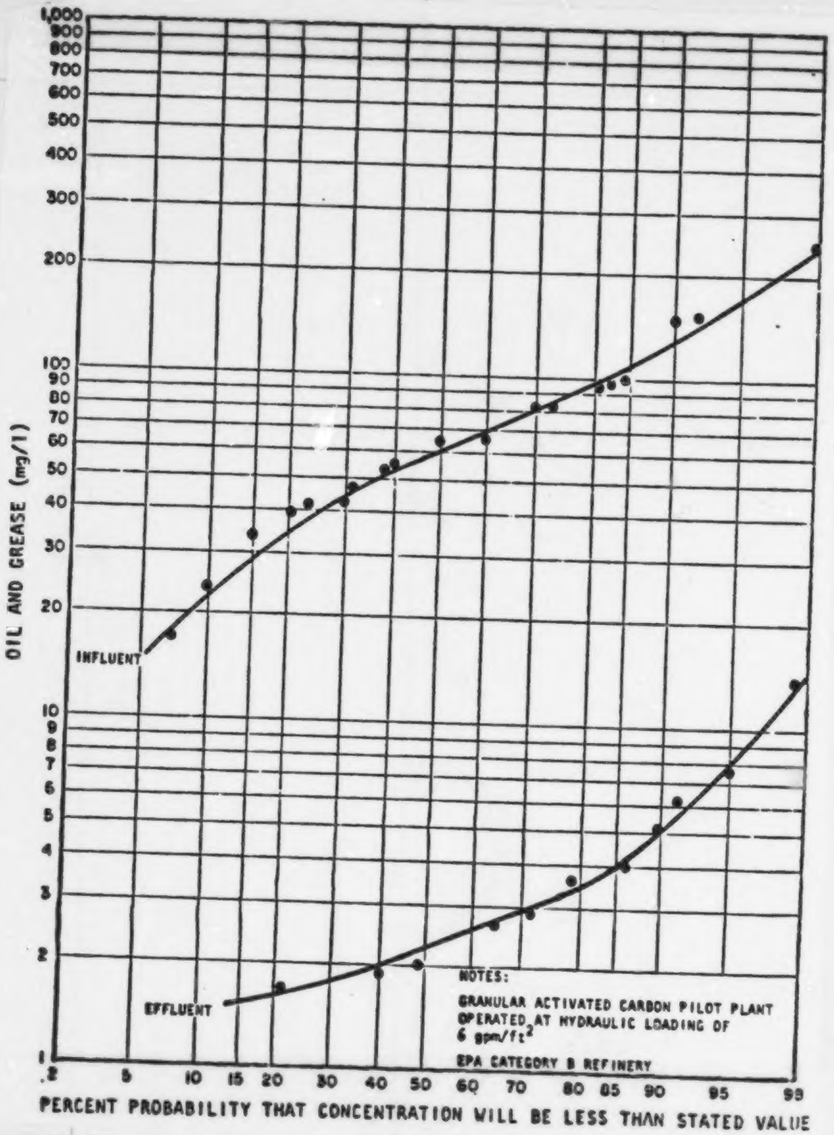

NOTES:

GRANULAR ACTIVATED CARBON PILOT PLANT OPERATED AT HYDRAULIC LOADING OF 6 gpm/ft^2

EPA CATEGORY B REFINERY

FIGURE 27. Variation in GAC treatment performance for oil and grease removal from API separator effluent.

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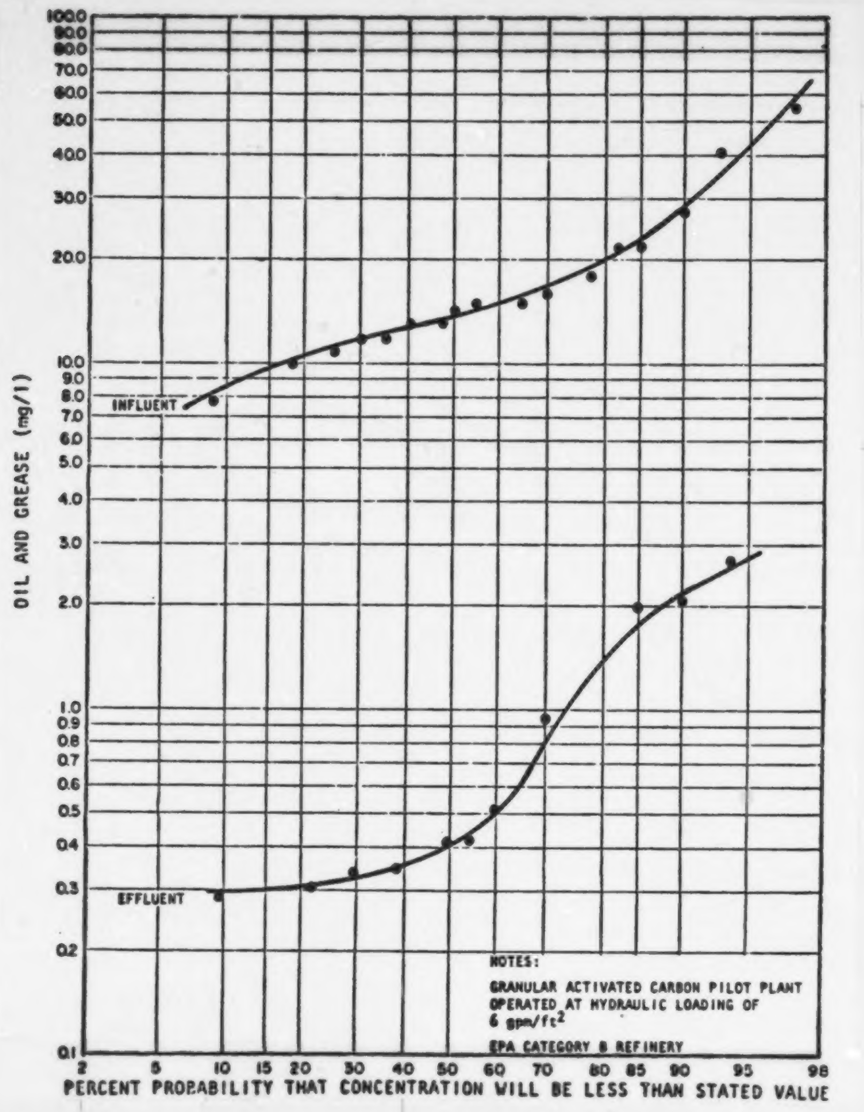

FIGURE 28. Variation in GAC treatment performance for oil and grease removal from aerated lagoon effluent.

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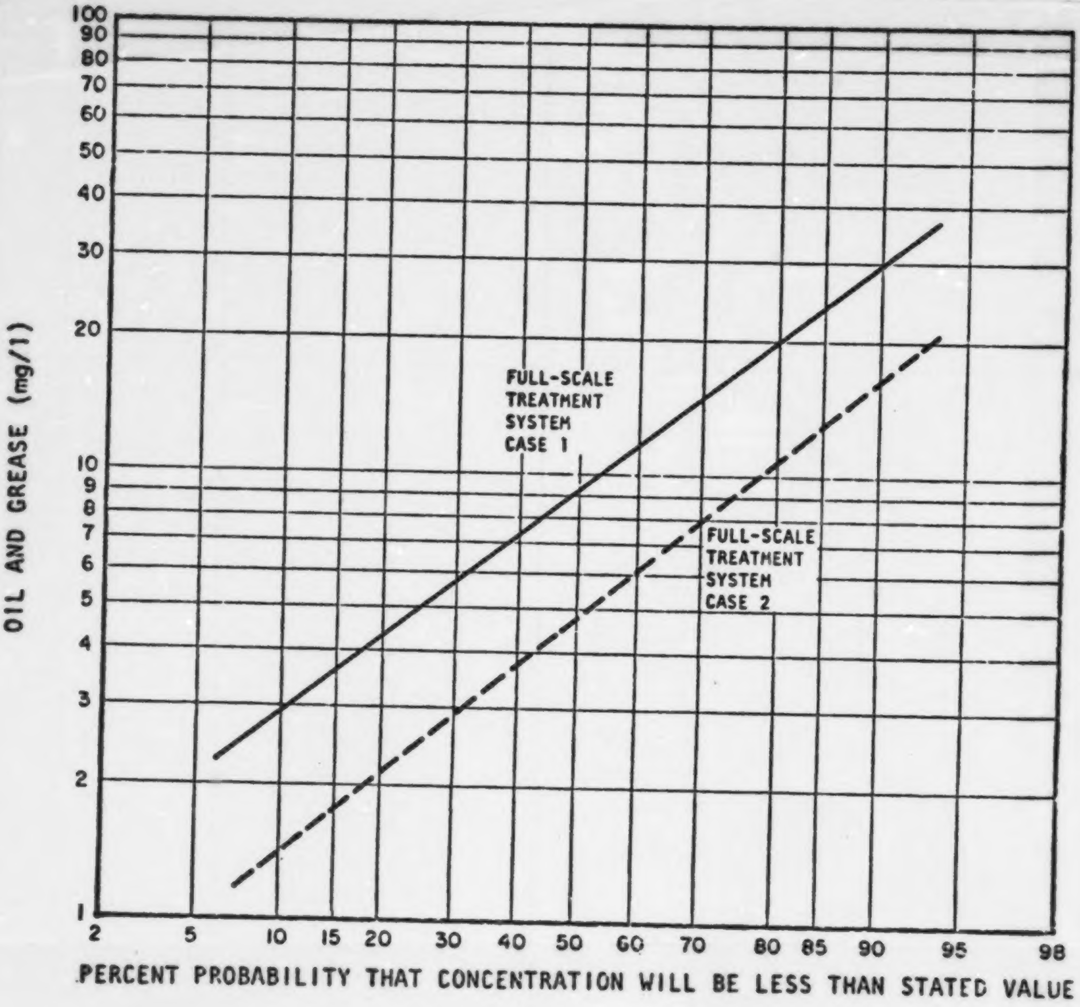

FIGURE 29. Effluent oil and grease from GAC unit processes for the treatment of refinery wastewaters

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report. The specific constituent nature of the sludges is adequately described elsewhere[188,204].

Sludges from refinery operations and waste treatment processes can be handled in numerous ways. Historically, the method most often used was lagoon storage of sludges with ultimate disposal of the combustible material. As land resources diminished, the necessity for concentration of sludges prior to disposal became apparent. In general, the methods of sludge concentration vary with the type of sludge. Oily sludges from storage tanks and oil-water separator bottoms can be concentrated by precoat vacuum filtration or centrifugation. These methods permit a certain amount of oil recovery from the sludges and such recovery is warranted considering the quantity of oil likely to be present in gravity separator bottoms. A characterization of oil contaminated sludges from both an API separator and a TPS unit is presented in Tables 21 and 22, respectively. These data indicate that a greater amount of oil can be found in API separator bottoms than in TPS sludges; nevertheless, a significant quantity of oil is present in the sludges from both of these units.

Sludges from boiler treatment blowdown and chemical or biological treatment of refinery wastewaters also can be thickened and subsequently dewatered by vacuum filtration or centrifugation. The ultimate disposal of dewatered sludge is normally either by incineration, landfill/landfarming, or ocean disposal. Acid and caustic sludges from refinery processes generally require neutralization before dewatering and ultimate disposal.

The only available method of disposal for spent treating clays and cracking/desulfurization catalysts is landfilling due to the potentially hazardous nature of these materials. Some refineries have reported landfarming of spent clays, although this method is unacceptable in areas where the soils have a relatively high permeability and would run the risk of groundwater contamination. The spent clays and catalysts should be considered hazardous solid wastes and should be disposed of in accordance with proper hazardous material landfill procedures. Cooling tower sludges can be landfarmed or landfilled, providing that neither chromate nor zinc is present. If these constituents are present in the sludge in significant concentrations, this would preclude the use of landfarming as a disposal method. Consequently, some cooling tower sludges must be disposed of in a hazardous material landfill[205].

With the exception of incineration and digestion where waste solids are actually destroyed, the majority of existing solids handling processes are oriented toward the concentration of sludges. Since the economics of ultimate disposal are predicated on the volume of sludge handled, the concentration of waste solids can result in definite cost savings. The most common sludge dewatering processes are: (1) rotary drum vacuum filtration; (2) pressure filtration; and (3) centrifugation.

Vacuum filters are the most widely used type of mechanical sludge dewatering device for the concentration of wastewater sludges. It is a filtration process in which solids are separated from the liquid phase by means of a porous media which retains the

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TABLE 21. CHARACTERIZATION OF OIL CONTAMINATED API SEPARATOR BOTTOMS*

API Separator Samples (grab)	Oil Free Dry Solids Percent Weight	Oil Free Volatile Dry Solids Percent Weight	Oil Percent Weight	Ratio of Oil To Oil Free Dry Solids	Total Sulfur Percent
1	6.6	2.1	16.5	2.5	-
2	9.2	2.7	5.7	0.6	0.2
3	2.5	1.1	34.0	13.5	-
4	14.5	4.1	4.5	0.3	0.4
5	9.9	3.1	5.8	0.6	4.6
6	15.1	4.0	1.9	0.1	0.7
7	13.1	4.9	8.0	0.6	0.7
8**	26.5	3.7	31.7	1.2	1.2

*EPA Category E Refinery.

**Composite taken over 24 hours.

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TABLE 22. CHARACTERIZATION OF OIL AND SLUDGE PHASES FROM TILTED-PLATE SEPARATOR*

	Oil Phase			Sludge Phase			
Case	Percent Sediment Volume	Percent Oil Volume	Specific Gravity of Oil	Percent Sediment Volume**	Percent Oil Volume	TSS (mg/l)	VSS (mg/l)
1	5.0	87	-	11	2	25,000	21,000
2	6.0	82	0.921	14	2	57,000	45,000
3	11.5	86	0.897	25	5	-	-
4	3.0	85	0.905	9	6	-	-
5	0.5	99	-	-	-	-	-

*These data are characteristic of a pilot scale tilted-plate separator treating petroleum refinery wastewater

**The sludge phase exhibited an average dry solids content of four percent by weight.

solids but allows the liquid to pass through. Media employed for this purpose include nylon, dacron, polyethylene cloth, steel mesh, or tightly-wound steel coils. The filtration process is accomplished by means of a horizontal drum covered with filter media which rotates in a tank with approximately one quarter or more of the drum submerged in wet sludge. As the drum rotates, a vacuum is applied on the inner side of the filter media which draws water from the sludge and produces a moist cake of solids on the outer surface which is removed prior to re-entering the tank. Precoats are often used to speed filtration rates or collect more of the fine particles in the slurry. The principal sludge properties which affect vacuum filtration dewatering are: (1) solids concentration; (2) viscosity; (3) compressibility; and (4) chemical characteristics.

The filter press, which is the simplest of all pressure filters, is an assembly of alternate solid plates, the faces of which are grooved to permit drainage. Between these plates rest hollow spaces in which the cake collects during filtration. A filter medium, usually some sort of fabric, covers both faces of each plate and cake formation occurs on each face. Filter presses can operate at pressures up to 1,000 psia. Water and oils are able to pass through the filter medium while solids are retained on the fabric. Data from a pilot-scale filter press unit used to dewater oily solid wastes are presented in Table 23. Filter cake solids concentrations range from a low of 40 percent by weight to a high of 71 percent, depending on the nature of the filtration aid applied during operation. The sludge properties which affect filter press dewatering are the same as those which impact upon vacuum filtration process efficiency.

Centrifugation permits the mechanical dewatering of sludges through centrifugal force. Within a centrifuge, centrifugal force acts on a sludge particle causing it to settle through the liquid. The variables which affect gravity sedimentation also affect sedimentation within centrifuges; namely, particle size, density differential, and liquid viscosity. Sludge solids in suspension are a combination of particles both granular and fibrous in nature. Extremely fine particles which will not settle under normal gravity conditions will separate at higher gravitational forces. In general, those sludges which separate most readily and concentrate to a fair degree during plain sedimentation will dewater most efficiently by centrifugation. The introduction of flocculation aids, such as polymers, has increased the range of materials that can be satisfactorily dewatered by centrifuges. The degree of solids capture can be regulated over a wide range by adjusting the amount of chemical coagulant applied during dewatering. Data from a pilot-scale vertical solid bowl centrifuge unit used to dewater oily solid wastes are presented in Table 24. Bowl cake solids concentrations range from a low of 43 percent by weight to a high of 62 percent, depending on operating conditions. The sludge dewatering performance levels for the centrifugation process were comparable to that observed with the filter press unit.

Landfarming of organic, biodegradable petroleum refinery solid wastes is an environmentally sound solid waste management practice when careful consideration is given to site selection, solids, topography, and surrounding land uses in order to minimize adverse impacts that could arise from the operation. The types of soils usually considered best suited for waste disposal by landfarming are those that contain high proportions of

TABLE 23. PILOT-SCALE FILTER PRESS UNIT FOR DEWATERING OILY SOLID WASTES[a]

Sludge Feed Mixture[b]	Filtration Aid (lb clay per lb dry solids)	Chemical Addition (lb/gal)[c]	Process Temperature (°F)	Cycle Time (hours)	Feed		Cake		
					Percent TSS	Percent Oil	Percent TSS	Percent Oil	Cake Calorific Value (BTU/lb)
1	0.6	0.12	175	2	12	8.5	50	17.5	4,700
2	0.6	0.12	50	2	12	8.5	40	20.0	-
3	0.6	-	175	2	23	12.3	54	13.0	-
4	0.6	0.06[d]	140	2	23	12.0	46	15.0	-
5	0.6	0.06[d]	100	2	23	5.9	61	6.4	3,030
6	0.56	0.07	100	2	19	-	57	8.7	4,590
7	0.56	0.07	100	1	17	-	58	10.1	2,900
8	0.56	0.07	100	2	17	-	61	4.9	-
9[e]	2.5[f]	0.10	60	2	16	-	71	-	-
10[g]	0.57	0.065	178	2	15	16.4	58	7.1	3,290
11	3.2	-	180	2	39	22.7	61	11.9	3,720

[a] EPA Category E Refinery.

[b] Refinery oily sludge mixture consisted of contaminated API separator sludge, leaded and nonleaded gasoline storage tank bottoms and oil free sludge material.

[c] Lime

[d] Spent caustic

[e] Uncontaminated API Separator sludge

[f] Spent catalyst

[g] Thickened IAF float solids

TABLE 24. PILOT-SCALE VERTICAL SOLID BOWL CENTRIFUGE UNIT FOR DEWATERING OILY SOLID WASTES - EPA CATEGORY E REFINERY

Feed				Centrate			Cake	
Sludge Feed Mixture*	Operating Conditions**	Percent TSS	Percent Oil	Percent TSS Recovery	Percent Oil Recovery	Percent TSS	Percent TSS	Percent Oil
1	-	8.3	5.4	98	99	0.2	53.8	0.3
2	lime addition	9.5	11.9	82	97	1.8	54.9	3.4
3	emulsion breaking chemical	9.0	26.5	86	99	1.3	56.0	2.5
4	-	10.3	15.2	81	99	2.0	62.4	0.9
5	-	9.4	22.0	78	99	2.1	59.0	1.2
6	-	11.0	10.5	88	94	1.4	60.3	4.5
7†	unheated feed	8.5	-	96	-	0.34	54.4	-
8††	-	1.0	0.8	95	98	0.50	42.7	0.7

*Refinery oily sludge mixture consisted of contaminated API separator sludge, leaded and unleaded gasoline storage tank bottoms and oil free sludge material.

**Feed heated to 175°F.

†Uncontaminated API bottoms.

††Thickened IAF float solids.

clay and organic matter to adsorb and filter the applied waste material. Wastes to be landfarmed should contain organic constituents that are susceptible to biodegradation and not subject to significant leaching while the degradation process proceeds. In general, refinery oily solid wastes and waste treatment biosolids meet these requirements.

The rate and extent of biodegradation of waste in the soil is strongly influenced by many chemical and physical factors. Some of the principal factors controlling biodegradation are: (1) the composition of the waste; (2) contact between waste and soil microorganisms; (3) presence of adequate oxygen; (4) soil temperature; (5) soil pH; (6) presence of available inorganic nutrients; and (7) moisture content of the soil. The presence of adequate oxygen in the soil is essential to effective biodegradation. Aerobic biodegradation of organic matter is much more rapid and complete than is anaerobic waste stabilization. Generally, adequate drainage and proper waste loading will prevent anaerobic conditions.

The presence of available nitrogen and phosphate in the soil is essential to achieve the maximum biodegradation rate. These nutrients are normally supplied by common agricultural fertilizers. The amounts required are dependent on available nitrogen and phosphate in the waste, fertilizer persistence in the soil, rate of waste application, and waste biodegradation rate.

Data from pilot-scale landfarm plots treating oily solid wastes are presented graphically in Figure 30. These data, which depict both fertilized and unfertilized conditions, indicate that the removal of oil and grease by landfarming is represented by first-order kinetics. Namely, that the fraction of oil and grease remaining in the soil of the landfarm site (F) is directly proportional to the time elapsed since the initial application (t) as follows:

$$F = e^{-kt} \qquad (4)$$

where k is the first-order rate constant. The rate constant may be obtained from the slope of the line of best fit as is indicated in Figure 30. The impact of fertilization upon oil and grease biodegradation rate is apparent from these data.

The application rate of 800-960 barrels of sludge per acre per year is considered acceptable for landfarming oily sludges from refinery operations and ballast waste treatment. It is recommended that groundwater quality in the landfarm area be monitored periodically. If deterioration is observed, the application rate is generally reduced to a level which precludes further contamination. Due to the potentially high salt content of ballast oily solids, however, it is necessary to elutriate these sludges before landfarming. It is acceptable to mix together the elutriated ballast solids and the refinery sludges in a single landfarming operation.

Landfilling also is an acceptable treatment process for final disposal of petroleum refinery oily process and ballast water sludges. Landfilling consists of the basic operations of dumping, spreading, compacting, and covering waste solids which are classified either

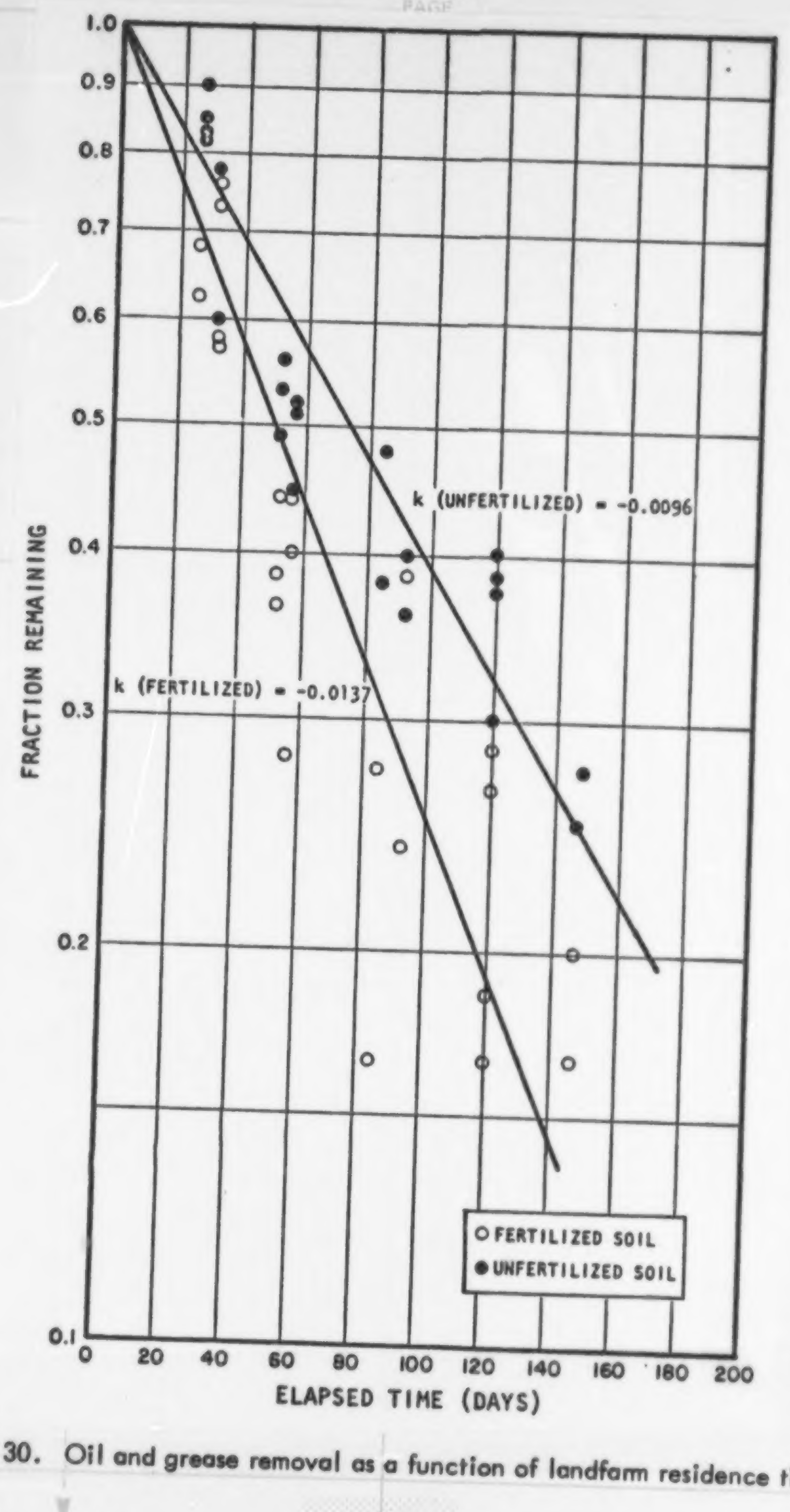

FIGURE 30. Oil and grease removal as a function of landfarm residence time

hazardous or nonhazardous. The sludge classification will ultimately determine the procedures and requirements for safe disposal of the various solid wastes. Usually, landfill sites are located in thick, relatively impermeable formations such as massive clay beds. Soils with a high clay and silt content also are acceptable as landfill sites. Artificial impermeable liners will be required for most hazardous solid wastes, as well as other precautionary measures such as landfill monitoring and leachate collection systems.

A two-level leachate collection system is usually installed beneath a pit, pond, or earthen facility receiving hazardous wastes. The primary level of protection consists of an impermeable synthetic liner which is, in turn, protected by a layer of permeable washed sand. A network of perforated pipes is usually placed immediately above the primary liner to facilitate leachate collection. A secondary barrier of compacted clay will usually underlie the primary barrier and serve as further protection for underlying groundwater. The disposal site also will include groundwater-quality monitoring wells, and the performance of the leachate management system is usually monitored on a regular basis.

Oily sludges from gravity oil-water separators and tank bottoms (other than leaded) may be either landfarmed or landfilled. Any leaded tank bottom sludges will have to be disposed of in a hazardous material landfill in order to prevent potential groundwater contamination from the leaching of lead. Landfarming rather than landfilling is the recommended disposal method for all oily sludges including air flotation float material produced in a refinery wastewater treatment plant. In general, oily sludges other than leaded tank bottoms have been successfully degraded by the landfarming process[205]. The analysis of soil from experimental landfarm sites used for the disposal of oily solid wastes is presented in Table 25. Data from these experimental plots which are operated both with and without fertilizer addition to the soils indicate that slight increases in the quantity of lead, nitrate, and chromium have occurred over the test period. Major increases in the quantity of ammonia, potassium, and sulfate present in these soils also are evident. These increases are due, in part, to the fertilization process. The storm water runoff and leachate characteristics from the experimental landfarm sites are presented in Table 26. These data illustrate the need for proper runoff and leachate collection measures at a landfarm site in order to minimize any harmful effects to the environment.

Incineration is used to reduce the volume of a solid waste by combustion to an ash, which is subsequently landfilled. At present, it is costly in comparison to other land disposal methods and normally only is feasible where available land is scarce. A primary consideration in the cost-effectiveness of sludge incineration is the effect of sludge feed composition on auxiliary fuel requirements. The heat yield of a given sludge is a function of the relative amounts and elemental composition of the contained combustible elements. Pretreatment methods such as chemical conditioning and dewatering result in a substantial reduction in incineration fuel requirements, but at the expense of creating increased energy demands on other unit processes. The combustibility of a sludge is dependent on the volatile content of the sludge. The inert content of the feed sludge will reduce its heat value and effect the requirements for complete combustion.

TABLE 25. ANALYSIS OF SOIL FROM LANDFARM SITES FOR THE DISPOSAL OF OILY SOLID WASTES

Parameter	Control*	Experimental Plot With Fertilizer**	Experimental Plot Without Fertilizer**
pH	7.7	6.2	7.0
Organic Matter, lb/acre***	0.25	3.75	3.6
Cation Exchange Capacity, meq/100 g	1.66	6.13	4.15
Chlorides, meq/100 g	2.1	2.7	2.1
Sulfate, lb/acre	Nil	>250	>250
Nitrate, lb/acre	2	18	22
Ammonia, lb/acre	5	25	7
Potassium, lb/acre	25	285	25
Cadmium, mg/l	<0.0015	<0.02	<0.02
Chromium, mg/l	<0.003	3.96	3.54
Lead, mg/l	<0.015	0.9	1.28
Mercury, mg/l	Nil	-	-
Nickel, mg/l	<0.01	0.14	<0.1
Zinc, mg/l	0.1	5.5	4.8

*Lime applied.

**Lime applied; total oil and grease load = 3.35 lb/ft^2.

***The lb/acre represents seven inches of soil over one acre.

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TABLE 26. STORM WATER RUNOFF AND LEACHATE CHARACTERISTICS FROM A LANDFARM SITE FOR THE DISPOSAL OF OILY SOLID WASTES

Parameter	Site Runoff From Experimental Plot*	Forced Leachate From Experimental Plot**	Forced Leachate From Control
pH	5.8	6.5	7.2
BOD_5, mg/l	406	174	35
COD, mg/l	1,041	1,304	40
Oil and Grease, mg/l	Nil	Nil	Nil
TOC, mg/l	268	295	13
Chlorides, mg/l	201	380	5
Sulfate, mg/l	Nil	4	4
Ammonia, mg/l	27	140	Nil
TDS, mg/l	1,950	4,950	122
Cadmium, mg/l	Nil	<0.0015	<0.0015
Chromium, mg/l	<0.003	<0.003	<0.003
Lead, mg/l	Nil	<0.015	<0.015
Mercury, mg/l	<0.002	-	-
Nickel, mg/l	Nil	<0.1	<0.01
Zinc, mg/l	0.38	0.21	<0.001

*Fertilized test plot; total oil and grease load = 3.35 lb/ft^2.

**Leachate data taken from laboratory test core obtained from the experimental plot in which deionized water was poured through the sample under pressure.

Incineration is a two-step process involving both drying and combustion. The drying step essentially involves some form of mechanical dewatering which reduces the moisture content of the sludge to within a range where the heat required to evaporate the remaining water within the solid mass nearly balances the available heat from combustion of dry solids. The practical limit for mechanical dewatering is normally between 50 and 60 percent moisture which is not sufficient to sustain the combustion reaction; consequently, the remaining portion of the drying sequence which occurs in the incinerator will require auxiliary fuel addition. Self-sustained combustion is often possible with dewatered raw sludges once the burning of auxiliary fuel raises incinerator temperatures to the ignition point.

PROCESS PERFORMANCE VARIABILITY

Candidate wastewater treatment, solids handling, and disposal processes are presented schematically in Figures 31, 32, and 33. Considering these schematic drawings, it is apparent that a multitude of sequential process permutations are possible, ranging from direct contract disposal to a complex system involving primary, secondary, and tertiary wastewater treatment, conditioning, dewatering, incineration, and ultimate disposal of sludges. Selection of the optimum process or system is usually based primarily on economic considerations. Moreover, since the economics of disposal are contingent upon such dynamic factors as landfill availability and regulatory criteria, the system must be flexible enough for modification. Therefore, the optimum disposal system should provide for a least-cost solution which ultimately allows for the efficient implementation of future expansions as dictated by treatment objectives.

Regardless of the type of wastewater or waste solids processing system finally implemented, a residual of material will require ultimate disposal to either a landfarm, landfill, or some other treatment option. Moreover, the implementation of a solids handling process requires a decision as to whether it is necessary to continue further solids processing or take the option of contract disposal. For instance, aerobic or anaerobic digestion presents an alternative process for solid waste handling. Such processes not only reduce the volume of degradable solids, but the remaining solids also are less susceptible to the production of noxious odors and are rendered more amenable to several of the potential dewatering processes. Since waste activated sludge is the only waste solid category presented in Figure 30 which is subject to biodegradation by digestion, it would constitute the only feed to a digester. However, landfarming can be used to dispose of waste biological solids and oily process sludges which makes it a more favorable sludge disposal alternative.

It is axiomatic that biological, chemical, or physical wastewater treatment processes produce effluents of varying quality and this inherent variability cannot be significantly altered by in-plant control, operational changes, or changes in concept and design. Although effluent variability is common to all wastewater treatment processes, it is most noticeable with biological systems. The variability in effluent quality from a properly designed and operated biological treatment system is attributable to the basic nature of the treatment process, the raw waste load characteristics, and geographical and

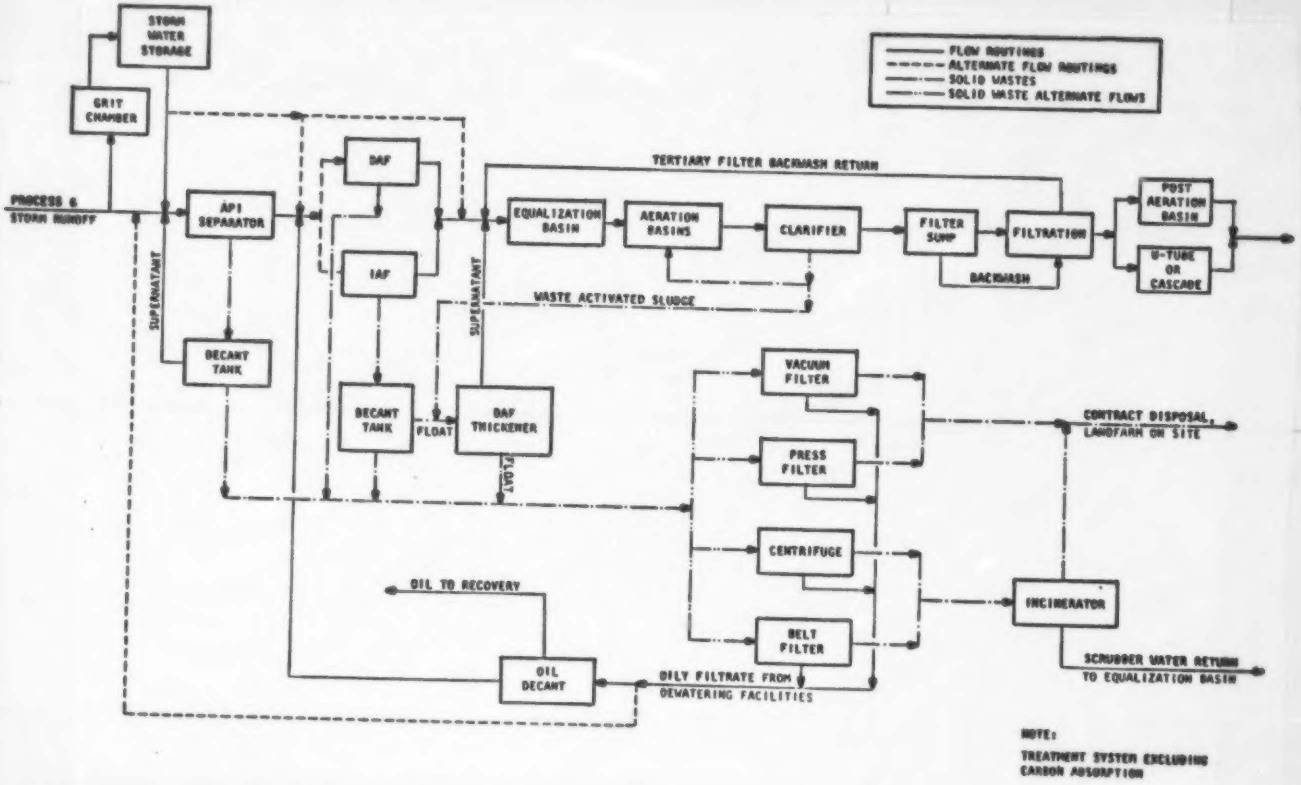
FLOW ROUTINGS
ALTERNATE FLOW ROUTINGS
SOLID WASTES
SOLID WASTE ALTERNATE FLOWS
STORM WATER STORAGE
GRIT CHAMBER
PROCESS & STORM RUNOFF
API SEPARATOR
SUPERNATANT
DECANT TANK
DAF
IAF
DECANT TANK
FLOAT
DAF THICKENER
FLOAT
SUPERNATANT
TERTIARY FILTER BACKWASH RETURN
EQUALIZATION BASIN
AERATION BASINS
CLARIFIER
WASTE ACTIVATED SLUDGE
FILTER SUMP
FILTRATION
BACKWASH
POST AERATION BASIN
U-TUBE OR CASCADE
VACUUM FILTER
PRESS FILTER
CENTRIFUGE
BELT FILTER
CONTRACT DISPOSAL, LANDFARM ON SITE
INCINERATOR
SCRUBBER WATER RETURN TO EQUALIZATION BASIN
OIL TO RECOVERY
OIL DECANT
OILY FILTRATE FROM DEWATERING FACILITIES
NOTE:
TREATMENT SYSTEM EXCLUDING CARBON ADSORPTION

FIGURE 31. Petroleum refinery wastewater treatment plant schematic.

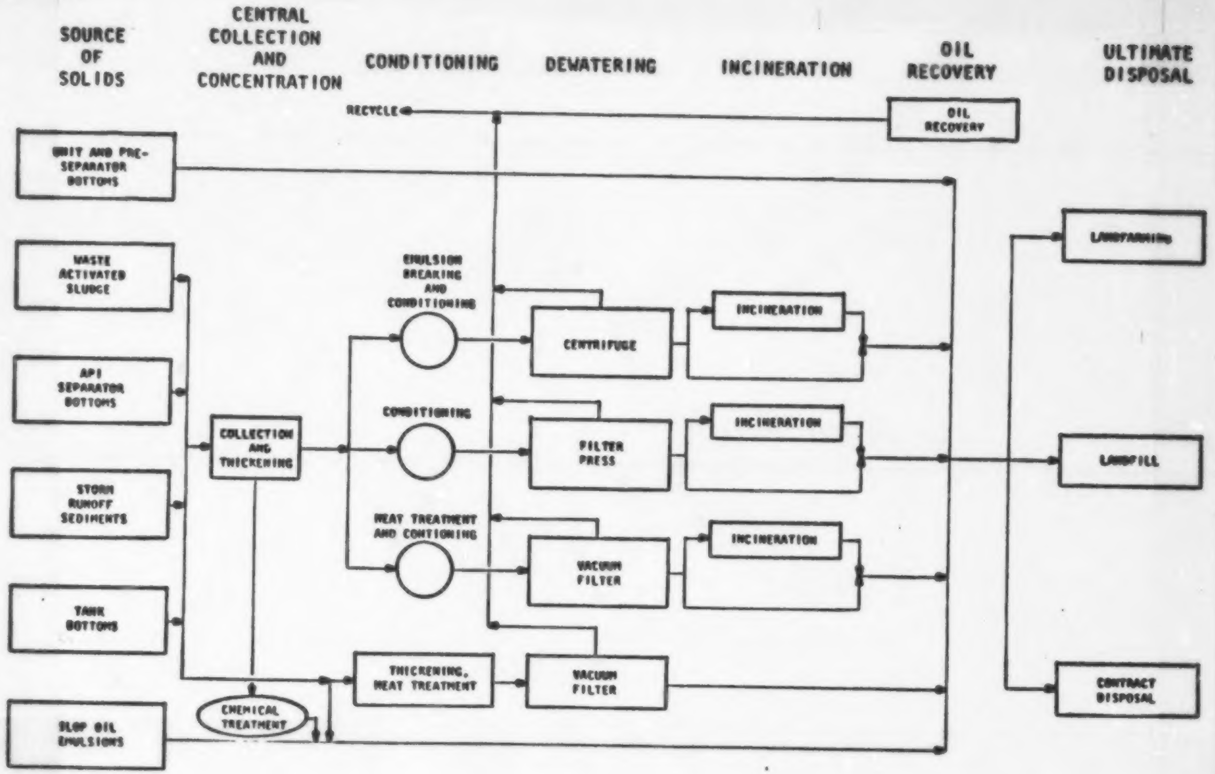
SOURCE OF SOLIDS
CENTRAL COLLECTION AND CONCENTRATION
CONDITIONING
DEWATERING
INCINERATION
OIL RECOVERY
ULTIMATE DISPOSAL
RECYCLE
OIL RECOVERY
UNIT AND PRE-SEPARATOR BOTTOMS
WASTE ACTIVATED SLUDGE
API SEPARATOR BOTTOMS
STORM RUNOFF SEDIMENTS
TANK BOTTOMS
SLOP OIL EMULSIONS
COLLECTION AND THICKENING
CHEMICAL TREATMENT
EMULSION BREAKING AND CONDITIONING
CONDITIONING
HEAT TREATMENT AND CONTIONING
THICKENING, HEAT TREATMENT
CENTRIFUGE
FILTER PRESS
VACUUM FILTER
VACUUM FILTER
INCINERATION
INCINERATION
INCINERATION
LANDFARMING
LANDFILL
CONTRACT DISPOSAL

FIGURE 32. Schematic of solids handling and disposal alternatives.

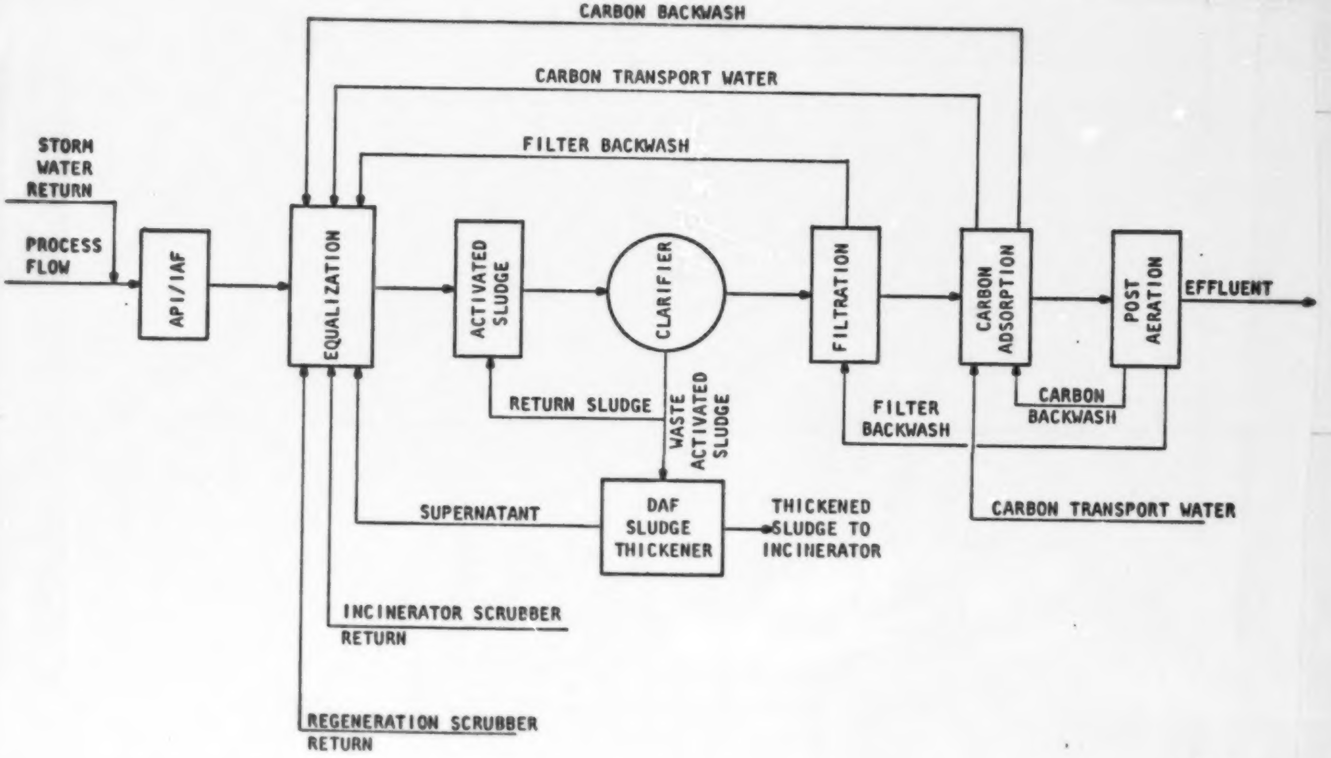
CARBON BACKWASH
CARBON TRANSPORT WATER
FILTER BACKWASH
STORM WATER RETURN
PROCESS FLOW
API/IAF
EQUALIZATION
ACTIVATED SLUDGE
CLARIFIER
FILTRATION
CARBON ADSORPTION
POST AERATION
EFFLUENT
RETURN SLUDGE
WASTE ACTIVATED SLUDGE
FILTER BACKWASH
CARBON BACKWASH
DAF SLUDGE THICKENER
SUPERNATANT
THICKENED SLUDGE TO INCINERATOR
CARBON TRANSPORT WATER
INCINERATOR SCRUBBER RETURN
REGENERATION SCRUBBER RETURN

FIGURE 33. Tertiary carbon adsorption addition to petroleum refinery wastewater treatment plant.

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climatological conditions. This is the minimum variability which can be practically obtained assuming proper system design, management, and operational control.

A change in feedstock will result in raw waste load variations which impact upon biological treatability. Both the quantity and quality of the raw waste load are functions of such crude oil properties as specific gravity as well as sulfur, nitrogen, and trace metal content. Changes in product mix and product specifications have a similar effect. The reduction of wastewater flow from production units normally results in higher influent concentrations of organic constituents to the treatment facility. Since most transitory loads from refinery processes cannot be completely sequestered, the cyclic changes in raw waste loads will result in effluent quality variation. Events such as turnarounds, production of specialty items, changes in calendar production patterns, and contrasts in dry-weather and wet-weather operations impact on the variability range. Included with the aforementioned items are the effects due to inordinate dumps or spills and poor housekeeping practices. Nevertheless, the impact of raw waste load variation can be minimized by in-plant changes or by installing equalization, surge, and off-specification impoundment capacity in front of biological treatment processes.

The impact of temperature on biodegradation rate and its subsequent effect on biological treatment variability is primarily evident on a long-term or seasonal basis. The actual degree of variability is not only attributable to water temperature, but also to the nature and complexity of the wastewater. The performance of an activated sludge system is more subject to temperature fluctuations when treating soluble organic materials. This is attributed, in part, to the temperature-sensitive nature of biochemical reactions which are responsible for the removal of soluble organics, rather than the "biosorption" mechanisms which remove colloidal or suspended organic matter.

Effluent TDS variability is a function of the varying discharges of process wastewater as well as the changes in cooling tower or boiler blowdown and the cyclic treatment of contaminated ballast water and storm water runoff. Biological treatment systems normally function more efficiently when treating low dissolved solids wastewaters and abrupt changes will have a pronounced deleterious effect on system performance. This reduction in efficiency is often accompanied by a noticeable increase in effluent suspended solids discharged from the final clarifier. Additional factors which impact on effluent variability are pH, nutrient deficiency, low dissolved oxygen, or the presence of toxic and/or inhibitory substances in the bioreactor.

Calculated daily and monthly variability factors for treatment of petroleum refinery wastewaters are presented in Table 27 and Table 28, respectively[199]. A daily variability factor is defined as the ratio of that effluent concentration or loading which encompasses 99 percent of the expected daily variation to the long-term arithmetic average effluent, and a monthly variability factor is defined as the ratio of that effluent concentration or loading which encompasses 99 percent of the expected monthly variation to the long-term arithmetic average effluent. These data specify an average variability factor for each pollutant parameter as well as the range of anticipated values. A comparison of the variability factors for the various end-of-pipe treatment systems indicates

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TABLE 27. DAILY VARIABILITY FACTORS FOR TREATMENT OF PETROLEUM REFINERY WASTEWATERS

Parameter	Activated Sludge		Aerated Lagoon and Polishing Pond		Aerated Lagoon and Dissolved Air Flotation W/Chemical Addition		BPCTCA	Activated Sludge Sand Filtration*		Aerated Lagoon Mixed Media Filtration** W/Alum Addition	
	Range	Average	Range	Average	Range	Average		Range	Average	Range	Average
BOD	6.6-7.6	7.1	2.5-3.6	3.2	-[††]	5.0	3.2	-	4.7	NA[†]	NA
COD	3.7-5.0	4.3	1.8-2.4	2.1	NA	NA	3.1	-	4.3	NA	NA
TOC	-	3.5	NA	NA	NA	NA	3.1	NA	NA	NA	NA
TSS	4.5-5.2	4.9	2.3-2.7	2.6	-	2.3	2.9	-	4.2	NA	NA
Oil & Grease	3.9-5.4	4.7	2.9-6.1	4.5	-	3.6	3.0	-	3.5	NA	NA
Phenols	4.5-5.2	4.9	2.4-6.7	4.5	-	2.2	3.5	-	8.6	NA	NA
NH_3-N	9.5-10.9	10.2	2.8-3.4	3.1	-	3.2	3.3	-	7.2	NA	NA
Sulfide	-	5.5	NA	NA	NA	NA	3.1	NA	NA	NA	NA
Cr^T	-	4.6	NA	NA	NA	NA	2.9	NA	NA	NA	NA
Cr^{+6}	NA	NA	NA	NA	NA	NA	3.1	-	11.4	NA	NA

* Three day composite used to determine daily variability factor.

** Daily data not available.

[†] NA - Information not available.

[††] Dash indicates one set of values.

TABLE 28. MONTHLY VARIABILITY FACTORS FOR TREATMENT OF PETROLEUM REFINERY WASTEWATERS

	Activated Sludge		Aerated Lagoon and Polishing Pond		Aerated Lagoon and Dissolved Air Flotation W/Chemical Addition		BPCTCA	Activated Sludge Sand Filtration		Aerated Lagoon Mixed Media Filtration W/Alum Addition	
Parameter	Range	Average	Range	Average	Range	Average		Range	Average	Range	Average
BOD	2.2-4.6	2.8	1.7-2.2	2.0	-*	3.9	1.7	-	4.1	-	2.6
COD	1.5-2.7	1.9	1.4-2.1	1.8	NA**	NA	1.6	-	2.2	NA	NA
TOC	-	2.9	NA	NA	NA	NA	1.6	NA	NA	NA	NA
TSS	1.8-3.3	2.5	1.4-2.3	1.9	-	1.6	1.7	-	3.2	-	2.0
Oil & Grease	1.8-2.9	2.2	2.0-5.7	3.8	-	2.1	1.6	-	1.9	-	5.0
Phenols	1.4-3.6	2.5	2.2-4.1	3.1	-	1.7	1.7	-	3.2	-	NA
NH_3-N	2.1-4.1	3.4	1.7-2.6	2.2	-	2.0	1.5	-	6.2	-	NA
Sulfide	-	1.6	NA	NA	NA	NA	1.4	NA	NA	NA	NA
Cr^T	1.8-2.6	2.2	NA	NA	NA	NA	1.7	NA	NA	NA	NA
Cr^{+6}	NA	NA	NA	NA	NA	NA	1.4	-	2.9	NA	NA

* Dash indicates one set of values.

** NA - information not available.

that the effluent from an activated sludge system is more variable than that from an aerated lagoon and polishing pond. The lower effluent variability of the aerated lagoon/polishing pond system is attributable to the long hydraulic contact times required of such biological treatment units to obtain long-term effluent qualities comparable to those attainable with the activated sludge process. In general, an aerated lagoon/polishing pond system provides low effluent variability, although the control of suspended solids in these effluents is difficult. Moreover, aerated lagoons do not offer the same operational flexibility as activated sludge systems and may not meet long-term effluent quality specifications for BPCTCA conditions.

The calculated variability factors for the various pollution abatement systems indicated in Tables 27 and 28 are greater than the EPA variability factors specified in the Development Document for BPCTCA conditions[190,199]. The addition of a filtration unit after biological treatment does reduce the monthly variability. However, the magnitudes of the variability factors are still greater than those specified in the Development Document.

It should be recognized that the distribution of effluent concentrations or mass loadings is bounded at the lower end by the nonremovable portion of a particular wastewater constituent. Such a boundary does not exist at the upper end of effluent concentrations or loadings. Consequently, the effluent variability factor will increase as the effluent concentration or loading from a treatment system decreases. Moreover, those variability analyses which are based solely on concentration information ignore that variability present in mass discharge which is due primarily to variations in flow.

An examination of the variability factors for each pollution abatement system indicates that the variability may be high for one waste constituent and low for another in the same treatment process. This is undoubtedly related to the differences in constituent concentration present in different refinery wastewaters which can, in turn, be related to product mix and refinery complexity. These differences are often manifested in the form of different effluent qualities from two similar treatment systems receiving the same type of wastewater. These data illustrate the difficulty in keeping the daily and monthly maximum allowable effluent qualities from refinery wastewater treatment systems within the allowable variation limits set by EPA, even when long-term effluent quality constraints are attained.

SECTION 6

EVALUATION OF POLLUTANT LEVELS OF PETROLEUM REFINERY WASTEWATERS AND RESIDUALS

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INTRODUCTION

In 1978 the EPA awarded the University of Tulsa contract No. R-805 099 010 to develop an environmental assessment for petroleum refining: wastewaters and residuals. One portion of this assessment is the preparation of a state-of-the-art report on pollutant emission levels. Accordingly this section summarizes a careful search of the recent literature on emission loads; avenues of emission; and includes estimates of accuracy, precision, variance and causes of variance whenever possible.

WASTEWATER EMISSIONS

Wastewater emissions are discussed under two classifications: raw waste loads and treated effluent loads.

Raw Waste Loads

Raw waste loads are reported for most of the so-called "traditional" pollutants, and for several priority pollutants, primarily those (such as cyanide, phenol, mercury) which have been monitored extensively. Median raw waste loadings for the five subcategories of refineries were collected in a 1972 study conducted jointly by API and EPA[206]. In this study, the net raw waste loading was defined as the amount of a given contaminant added to intake water per unit volume of crude oil charge to a refinery[206]. The median concentration values of these pollutants based on the refineries studied are presented in Table 29 in units of p.t.b. of crude oil processed. Since an average value of gallons of wastewater produced per barrel of oil processed was also given, a simple conversion gives the results in mg/ℓ, as also reported in Table 29. In addition the following priority pollutants were included and the results are included in Table 29: cyanides, phenolics, copper, lead, and zinc.

TABLE 29. MEDIAN RAW WASTE LOADINGS FOR REFINERY SUBCATEGORIES A THROUGH E AS REPORTED IN API-EPA SURVEY[206]

Parameter[a]	Class[b,c]									
	A		B		C		D		E	
	lb/1000 bbl	mg/L	lb/1000 bbl	mg/L	lb/1000 bbl	mg/L	lb/1000 bl	mg/L	lb/1000 bbl	mg/L
gal/bbl	18.00		40.44		42.65		47.34		86.96	
BOD_5	2.92	19.4	38.29	113	57.99	163	59.79	151	129.40	178
COD	13.33	88.7	105.77	313	168.38	473	184.00	466	296.59	409
TOC	2.49	16.6	17.76	52.6	54.26	152	50.91	129	58.65	80.8
Oil & Grease	3.13	20.8	13.74	40.7	18.09	50.8	56.82	144	50.16	69.1
Phenolics	0.01	0.07	1.52	4.5	4.03	11.3	2.19	5.5	2.56	3.5
Suspended Solids	4.43	29.5	11.84	35.1	18.62	52.3	39.23	99.3	21.73	29.9
Dissolved Solids	103.49	689	210.66	624	186.04	523	200.12	506	299.28	412
Sulfides	0.03	0.20	0.34	1.00	0.71	2.00	0.02	0.05	1.40	1.93
Chromium	0.00	<0.07	0.03	0.09	0.19	0.53	0.06	0.15	0.31	0.43
Ammonia Nitrogen	0.34	2.3	7.79	23.1	16.95	47.6	8.39	21.2	16.55	22.8
Organic Nitrogen	0.04	0.27	2.39	7.10	2.29	6.40	2.85	7.20	4.38	6.0
Nitrate Nitrogen	−0.01	0.00	0.00	<0.03	0.00	<0.03	0.00	<0.02	−0.02	0.00
Acidity	−0.96	0.00	0.00	<0.03	0.00	<0.03	−0.26	0.00	−0.56	0.00
Alkalinity	0.53	3.5	12.35	36.6	33.81	95.0	32.94	83.4	53.04	73.1
Total Phosphate	0.02	0.13	0.08	0.24	0.20	0.56	0.19	0.48	0.19	0.26
Cyanide	0.00	<0.07	0.00	<0.03	0.05	0.14	0.03	0.08	0.00	<0.01
Chloride	15.75	105	65.34	194	76.37	214	67.43	171	50.69	69.8
Fe	0.06	0.40	0.22	0.65	0.25	0.70	0.06	0.15	0.27	0.37
Cu	0.00	<0.07	0.00	<0.03	0.00	<0.03	0.00	<0.02	0.01	0.01
Pb	0.00	<0.07	0.00	<0.03	0.01	0.03	0.00	<0.02	0.01	0.01
Zn	0.00	<0.07	0.07	0.21	0.06	0.17	0.03	0.08	0.03	0.04
Color		48		38.3		104		534		21.7
Turbidity		178		83.8		1064		122		41.2
Volatile Suspended Solids		15		19.8		23.8				
Conductance				1712		1312				
Nitrite Nitrogen		0.06		0.15		0.80		0.10		0.17
Total Kjeldahl Nitrogen		6.6		99.5		448		543		23.3
pH		8.2		8.0		8.4		8.1		7.8

[a] Units for all parameters are mg/L with the following exceptions: color (color units), turbidity (J.T.U.), conductance (µmho/cm), and pH (pH units).

[b] Values reported for color, turbidity, VSS, conductance, nitrite nitrogen, TKN, and pH were obtained from limited raw data reported in the appendices to this reference and do not represent averages based on all the refineries which made up the API-EPA survey.

[c] A negative value for a parameter in the lb/1000 bbl column represents a case in which the plant intake water concentration exceeded the raw waste load by the indicated amount, and was reported as a zero concentration in mg/L. A zero value in the lb/1000 bbl column was interpreted as meaning a loading of less than 0.01 lb/1000 bbl and so this limit was used to arrive at the mg/L value.

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In 1978 a Department of Energy (DOE)-EPA study determined the variation in trace organics concentrations across the wastewater treatment system of a typical Class B refinery[207]. In addition to the trace organics several traditional pollutants were monitored in the raw waste stream; these are included as part of Table 30, which also reports concentrations at several stages of treatment for this waste stream as well as for the intake water.

The organic analyses in the DOE-EPA study were performed by GC-MS on methylene chloride extracts of the wastewater samples. Three extracts were collected - a neutral extract, an acid extract, and a base extract. Water samples extracted and analyzed included the raw wastewater after DAF treatment, effluent from activated sludge (AS) treatment, and effluent from activated carbon (AC) columns. The details of the extraction and analysis procedures are contained in the report of the study[207]. The results, which indicated that 304 trace organic compounds were detected, are presented in Tables 31 through 37 for the neutral extracts, Table 38 for the acid extracts, and Tables 39 through 41 for the base extracts.

Evaluation of the emission levels of the priority pollutants was the purpose of a 1978 study by EPA and API[208,209]. Intake waters, wastewater feeds to biotreatment, and final effluent streams from 17 refineries were sampled and analyzed for the 129 substances on the EPA Priority Pollutant list. A summary of the data from this study is presented in Tables 42 through 45.

Treated Effluent Loads

Several sources of data on the effluent concentrations of various pollutants after differing modes of treatment are available.

In the DOE-EPA study which has been described previously, data were presented for effluents from an ACFC, MMF, and AC columns[207]. These data are presented in Tables 30 through 41.

In the 1972 API-EPA survey[206] data were collected to determine the median performance of AS treatment plants for five refineries - three Class B and two Class C. These data are summarized in Table 46.

Data for treated effluent loadings of priority pollutants from 17 refineries were reported as part of the 1978 API-EPA study[208]. Concentration ranges for the priority pollutants in treatment plant effluents are presented in Tables 42 through 44 described previously.

In addition, at six of the refineries considered in the above study[208], pilot-scale GAC results were obtained for several traditional pollutants as well as a number of priority pollutants. These results were reported in a separate document[209]. The inlet wastewaters to the carbon columns were treated using multimedia filtration, and results were obtained for both virgin and regenerated carbons. The data summarizing the ranges

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TABLE 30. AVERAGE INTAKE AND WASTEWATER EFFLUENT CONCENTRATIONS AFTER VARIOUS TREATMENT PROCESSES IN A CLASS B REFINERY[207]

		Concentration, mg/L			
Parameter	Intake	DAF[a]	FC[b]	MMF[c]	AC[d]
Oil & Grease	<10	24	<10	<10	<10
Cyanide	< 0.02	0.25	0.14	0.15	< 0.02
Phenol	0.02	3.9	0.02	0.02	< 0.01
COD	<15	150	48	44	<15
BOD	<10	103	17	17	<10
TOC	18	57	24	22	9
TSS	21	38	<10	<10	<10

[a] Raw wastewater after dissolved air flotation treatment in plant's full-scale treatment system.

[b] Effluent from activated sludge final clarifier of full-scale treatment system.

[c] Effluent from pilot-scale mixed-media filter.

[d] Effluent from pilot-scale activated carbon columns.

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TABLE 31. CONCENTRATION OF n-ALKANES IN THE NEUTRAL FRACTION OF THE DAF EFFLUENT FROM A CLASS B REFINERY AND PERCENT REMOVAL BY THE ACTIVATED SLUDGE AND ACTIVATED CARBON UNITS[207]

Compound	Concentration in DAF (ppb)	Percent Removal by Activated Sludge[a]	Percent Removal by MMF + AC
n-nonane	32	NM	ND
n-decane	128	99 +	ND
n-undecane	349	99 +	T
n-dodecane	544	99 +	98
n-tridecane	675	99 +	96
n-tetradecane	683	99 +	94
n-pentadecane	651	99 +	91
n-hexadecane	493	99 +	91
n-heptadecane	355	99 +	88
n-octadecane	261	99 +	87
n-nonadecane	205	99 +	88
n-eicosane	160	99 +	85
n-heneicosane	107	99 +	79
n-docosane	64	99 +	80
n-tricosane	61	99 +	83
n-tetracosane	43	99 +	79
n-pentacosane	32	99 +	70
n-hexacosane	27	99 +	78
n-heptacosane	19	99 +	T
n-octacosane	13	99 +	T
n-nonacosane	11	NM	T
n-triacotane	NM	T	T
n-heneitriacotane	NM	T	T

[a] Neutral fraction of final-clarifier effluent.

T Trace concentration present
NM Not measurable due to interferences
ND Concentration not detectable

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TABLE 32. CONCENTRATION OF CYCLOALKANES AND ALKANES OTHER THAN n-ALKANES IN THE NEUTRAL FRACTION OF THE DAF EFFLUENT FROM A CLASS B REFINERY AND PERCENT REMOVAL BY THE ACTIVATED SLUDGE AND ACTIVATED CARBON UNITS[207]

Compound	Concentration in DAF (ppb)	Percent Removal by Activated Sludge[a]	Percent Removal by MMF + AC
Alkanes			
C_{13}-Alkane	159	99 +	T
C_{13}-Alkane	77	99 +	ND
C_{14}-Alkane	196	99 +	T
C_{14}-Alkane	246	99 +	79
Pristane	157	99 +	78
Phytane	67	99 +	59
Cycloalkanes[b]			
	30	99 +	ND
	21	99 +	ND
	57	NM	ND
	31	99 +	ND
	41	99 +	ND
	29	99 +	ND
	27	99 +	ND
	71	99 +	ND
	42	99 +	ND
	43	99 +	ND

[a] Neutral fraction of final-clarifier effluent.

[b] Also includes alkenes; exact qualitative analysis was not made; the 10 entries represent 10 cycloalkane-alkene compounds.

T Trace concentration present
ND Concentration not detectable
NM Not measurable due to interferences

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TABLE 33. CONCENTRATION OF ALKYLATED BENZENES IN THE NEUTRAL FRACTION OF THE DAF EFFLUENT FROM A CLASS B REFINERY AND PERCENT REMOVAL BY THE ACTIVATED SLUDGE AND ACTIVATED CARBON UNITS[207]

Compound	Concentration in DAF (ppb)	Percent Removal by Activated Sludge[a]	Percent Removal by MMF + AC
Toluene*	101	99 +	84
Ethyl benzene*	35	99 +	67
p and m-Xylenes	187	99 +	77
o-Xylene	101	99 +	77
i-Propyl benzene	5	ND	ND
n-Propyl benzene	13	99 +	T
m-Ethyl toluene	93	99 +	71
o-Ethyl toluene	32	99 +	T
1,3,5-Trimethyl benzene	43	99 +	ND
1,2,4-Trimethyl benzene	176	99 +	45
1,2,3-Trimethyl benzene	96	99 +	60
n-Butyl benzene	8	T	ND
m-n-Propyl toluene	19	99 +	ND
o-n-Propyl toluene	13	99 +	ND
m-Diethyl benzene	13	T	ND
1,3-Dimethyl-5-ethyl benzene	29	99 +	ND
1,3-Dimethyl-4-ethyl benzene	37	99 +	ND
1,2-Dimethyl-4-ethyl benzene	43	99 +	ND
1,3-Dimethyl-2-ethyl benzene	16	ND	ND
1,2-Dimethyl-3-ethyl benzene	13	T	ND
1,2,4,5-Tetramethyl benzene	27	99 +	ND
1,2,3,5-Tetramethyl benzene	48	99 +	T
1,2,3,4-Tetramethyl benzene	64	99 +	51

[a] Neutral fraction of final clarifier effluent.

T Trace concentration present

ND Concentration not detectable

*An E.P.A. Priority Pollutant

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TABLE 34. CONCENTRATION OF INDAN AND TETRALIN AND RELATED COMPOUNDS AND THEIR ALKYLATED DERIVATIVES IN THE NEUTRAL FRACTION OF THE EFFLUENT FROM A CLASS B REFINERY AND PERCENT REMOVAL BY THE ACTIVATED SLUDGE AND ACTIVATED CARBON UNITS[207]

Compound	Concentration in DAF (ppb)	Percent Removal by Activated Sludge[a]	Percent Removal by MMF + AC
Indan	93	99 +	50
1-methyl indan	104	99 +	T
2-methyl indan	61	99 +	ND
Ethyl indan	27	T	ND
Dimethyl indan[b]	61	99 +	T
Dimethyl indan	11	ND	ND
Dimethyl indan	35	99 +	ND
Trimethyl indan	35	T	ND
Tetralin	11	ND	ND
Methyl tetralin	64	T	ND
Ethyl tetralin	27	99 +	ND
Dimethyl tetralin	21	T	ND
Ethyl styrene	19	ND	ND
Ethyl styrene	48	99 +	ND
C_3-Styrene[b]	19	T	ND
C_3-Styrene	72	99 +	ND
C_3-Styrene	21	99 +	ND
C_3-Styrene	53	99 +	ND

[a] Neutral fraction of final clarifier effluent.

[b] Several dimethyl indan and C_3-Styrene compounds were observed - see succeeding compounds. Reference 2 provides structures.

T Trace concentration present
ND Concentration not detectable

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TABLE 35. CONCENTRATION OF NAPHTHALENE AND ALKYLATED NAPHTHALENES IN THE NEUTRAL FRACTION OF THE DAF EFFLUENT FROM A CLASS B REFINERY AND PERCENT REMOVAL BY THE ACTIVATED SLUDGE AND ACTIVATED CARBON UNITS[207]

Compound	Concentration in DAF (ppb)	Percent Removal by Activated Sludge[a]	Percent Removal by MMF + AC
Naphthalene*	197	99 +	38
1-Methyl naphthalene	448	99 +	45
2-Methyl naphthalene	259	99 +	33
Ethyl naphthalene	77	99 +	56
Dimethyl naphthalene	192	99 +	38
Dimethyl naphthalene	NM	--	--
Dimethyl naphthalene	267	99 +	27
Dimethyl naphthalene	203	99 +	I
Dimethyl naphthalene	96	99 +	12
Dimethyl naphthalene	45	99 +	37
C_3-Naphthalene	24	99 +	T
C_3-Naphthalene	21	99 +	88
C_3-Naphthalene	160	99 +	92
C_3-Naphthalene	45	99 +	T
C_3-Naphthalene	37	99 +	T
C_3-Naphthalene	51	99 +	
C_3-Naphthalene	99	99 +	70
C_3-Naphthalene	125	99 +	61
C_3-Naphthalene	85	99 +	45
C_3-Naphthalene	80	99 +	T
C_3-Naphthalene	93	99 +	T

[a] Neutral fraction of final clarifier effluent

NM Not measurable due to interferences

T Trace concentration present

I Increase in concentration

*An E.P.A. Priority Pollutant

TABLE 36. CONCENTRATION OF ALKYLATED BENZOTHIOPHENES AND DIBENZOTHIOPHENES IN THE NEUTRAL FRACTION OF THE DAF EFFLUENT FROM A CLASS B REFINERY AND PERCENT REMOVAL BY THE ACTIVATED SLUDGE AND ACTIVATED CARBON UNITS[207]

Compound	Concentration in DAF (ppb)	Percent Removal by Activated Sludge[a]	Percent Removal by MMF + AC
Methyl benzothiophene	21	T	ND
Methyl benzothiophene	16	99 +	71
Methyl benzothiophene	13	99 +	ND
Methyl benzothiophene	32	99 +	83
Ethyl benzothiophene	11	99 +	ND
Dimethyl benzothiophene	11	99 +	ND
Dimethyl benzothiophene	16	99 +	ND
Dimethyl benzothiophene	8	99 +	ND
Dimethyl benzothiophene	8	99 +	ND
Dibenzothiophene	13	T(N)	ND

[a] Neutral fraction of final clarifier effluent.

T Trace concentration present

N Noisy, possibly due to column bleed

ND Concentration not detectable

TABLE 37. PNAs AND ALKYLATED PNAs OTHER THAN NAPHTHALENES IN THE NEUTRAL FRACTION OF THE DAF EFFLUENT FROM A CLASS B REFINERY AND PERCENT REMOVAL BY THE ACTIVATED SLUDGE AND ACTIVATED CARBON UNITS[207]

Compound	Concentration in DAF (ppb)	Percent Removal by Activated Sludge[a]	Percent Removal by MMF + AC
Phenanthrene/ Anthracene*	168	99+	53
Methyl phenanthrene	72	N	T
Methyl phenanthrene	80	N	T
1-Methyl anthracene	27	99+	T
2-Methyl anthracene	27	99+	T
C_2-Phenanthrene/ Anthracene	5	N	ND
C_2-Phenanthrene/ Anthracene	5	N	ND
C_2-Phenanthrene/ Anthracene	16	N	ND
C_2-Phenanthrene/ Anthracene	37	N	ND
C_2-Phenanthrene/ Anthracene	40	N	ND
C_2-Phenanthrene/ Anthracene	11	N	ND
Fluorene*	27	N	ND
Methyl fluorene	29	99+	ND
Methyl fluorene	35	99+	T
Methyl fluorene	16	99+	ND
Acenaphthene*	3	I	ND
Methyl acenaphthene	35	N	ND
Methyl acenaphthene	24	N	ND
Methyl acenaphthene	16	N	ND
Biphenyl	24	T(N)	T
Methyl biphenyl	19	T(N)	ND
Methyl biphenyl	11	T(N)	
Pyrene*	29	99+	76
$C_{17}H_{12}$ PNA (such as methyl pyrene)	11	99+	ND
Chrysene*	5	99+	ND
1,2-Benzanthracene	13	99+	ND

[a] Neutral fraction of the final clarifier effluent.

N Noisy, possibly due to unresolved interfering organics

T Trace concentration present

ND Concentration not detectable

I Increase in concentration

*An E.P.A. Priority Pollutant

TABLE 38. PHENOLS IN THE ACID FRACTION OF THE DAF EFFLUENT FROM A CLASS B REFINERY AND PERCENT REMOVAL BY THE ACTIVATED SLUDGE AND ACTIVATED CARBON UNITS[207]

Compound	Concentration in DAF (ppb)	Percent Removal by Activated Sludge[a]	Percent Removal by MMF + AC
Phenol*	22	ND	ND
Cresol	33	99 +	NM
p-Cresol	50	ND	ND
Ethyl phenol	4	ND	ND
Ethyl phenol	7	ND	ND
Dimethyl phenol*	29	ND	ND
2,3-Dimethyl phenol	16	99 +	ND
Dimethyl phenol*	8	ND	ND
n-Propyl phenol	1	ND	ND
i-Propyl phenol	2	ND	ND
i-Propyl phenol	4	ND	ND
i-Propyl phenol	10	ND	ND
i-Propyl phenol	1	ND	ND
i-Propyl phenol	1	ND	ND
n-Propyl phenol & Methyl ethyl phenol	4	ND	ND
n-Propyl phenol & Methyl ethyl phenol	<1	ND	ND
Methyl ethyl phenol	2	ND	ND
Methyl ethyl phenol	3	ND	ND
2,4,5-Trimethyl phenol	3	99 +	ND
Methyl ethyl phenol & C_4-Phenol	1	ND	ND
Methyl ethyl phenol & C_4-Phenol	<1	ND	ND
C_3 and C_4-Phenol	1	ND	ND
C_3 and C_4-Phenol	1	ND	ND
Diethyl phenol	1	ND	ND
Diethyl phenol	<1	ND	ND

[a] Acid fraction of the *final clarifier* effluent.
ND Concentration not detectable
NM Not measurable
*An E.P.A. Priority Pollutant

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TABLE 39. ALKYLATED PYRIDINES IN THE BASE FRACTION OF THE DAF EFFLUENT FROM A CLASS B REFINERY AND PERCENT REMOVAL BY ACTIVATED SLUDGE AND ACTIVATED CARBON UNITS[207]

Compound	Concentration in DAF (ppb)	Percent Removal by Activated Sludge[a]	Percent Removal by MMF + AC
Picoline	<1	-	-
Ethyl pyridine	<1	ND	ND
4-Ethyl pyridine	<1	93	ND
Lutidine	<1	ND	T
Lutidine	2	98	ND
Ethyl picoline	NM	NM	ND
2-Ethyl picoline	1	ND	ND
Ethyl picoline	6	ND	ND
2,4,6-Collidine	2	ND	ND
2,3,6-Collidine	<1	ND	ND
2,3,5-Collidine	<1	ND	ND
Collidine	<1	67	99
Collidine	2	ND	ND
C_3-Pyridine	<1	ND	ND
C_3-Pyridine	<1	ND	ND
Ethyl lutidine	1	ND	ND
Ethyl lutidine	<1	ND	ND
Ethyl lutidine	1	ND	ND
Ethyl lutidine	<1	ND	ND
Ethyl lutidine	<1	ND	ND

[a] Base fraction of the final clarifier effluent.

NM Not measurable due to interferences

ND Concentration not detectable

T Trace concentration present

TABLE 40. ALKYLATED QUINOLINES IN THE BASE FRACTION OF THE DAF EFFLUENT FROM A CLASS B REFINERY AND PERCENT REMOVAL BY ACTIVATED SLUDGE AND ACTIVATED CARBON UNITS[207]

Compound	Concentration in DAF (ppb)	Percent Removal by Activated Sludge[a]	Percent Removal by MMF + AC
Quinoline	6	ND	ND
Methyl quinoline	4	ND	ND
Methyl quinoline	1	ND	ND
Methyl quinoline	<1	ND	ND
Methyl quinoline	<1	85	ND
Methyl quinoline	2	ND	ND
Methyl quinoline	1	ND	ND
Ethyl quinoline	<1	ND	ND
Dimethyl quinoline	2	94	89
Dimethyl quinoline	1	ND	ND
Dimethyl quinoline	2	ND	ND
Dimethyl quinoline	<1	ND	ND
Dimethyl quinoline	2	92	ND
Dimethyl quinoline	1	ND	ND
C_3-Quinoline	2	97	ND
C_3-Quinoline	2	97	ND

[a] Base fraction of the final clarifier effluent.

ND Concentration not detectable

TABLE 41. ALKYLATED ANILINES IN BASE FRACTION OF THE DAF EFFLUENT FROM A CLASS B REFINERY AND PERCENT REMOVAL BY ACTIVATED SLUDGE AND ACTIVATED CARBON UNITS[207]

Compound	Concentration in DAF (ppb)	Percent Removal by Activated Sludge[a]	Percent Removal by MMF + AC
Aniline	27	99 +	T
o-Toluidine	29	NM	ND
Toluidine	10	NM	ND
N,N-Dimethyl aniline	<1	89	ND

[a] Base fraction of the final clarifier effluent.

T Trace concentration present

ND Concentration not detectable

NM Not measurable due to interferences

TABLE 42. CONCENTRATION RANGES OF PRIORITY POLLUTANTS - VOLATILE ORGANICS CATEGORY REPORTED IN API-EPA PRIORITY POLLUTANTS SURVEY[208]

Parameter (μg/L)	Refinery Category[a]									
	A		B		C		E		Category Undesignated	
	Bio. Eff.*1	Final Eff.*2	Bio. Eff.*1	Final Eff.*2	Bio. Eff.*1	Final Eff.*2	Bio. Eff.*1	Final Eff.*2	Bio. Eff.*1	Final Eff.*2
Chloromethane							<100->100	<10		
Methylene Chloride	> 50	>50	< 0.5->100	< 0.2- 60	10	10	>100	<40	4.9	8
Chloroform	< 5	< 5	< 0.3- 10	< 0.3- 16	< 10	<10	10- 15	<10	< 0.3	<0.3
Carbon Tetrachloride			<10	<10	< 10	<10				
Bromomethane							< 10	<10		
Dibromochloromethane							< 10- 107	<10		
Bromodichloromethane	< 10	<10	<10	<10	< 10	<10				
Bromoform			< 0.1-< 0.3							
1,1-Dichloroethane					< 10	<10				
1,2-Dichloroethane			< 1 -< 10	< 1 -<10	< 10	<10	< 10	<10		
1,1,1-Trichloroethane			< 0.3-< 10	< 0.3-<10	< 10	<10	< 10	<10		
1,1,2,2-Tetra-Chloroethane	> 50	<10					< 10	<10		
1,1-Dichloroethylene							< 10	<10		
Trans-1,2-Dichloroethylene	20	<10	< 0.7- 1	< 0.7						
Trichloroethylene			< 1 - 5	< 1 - 1	< 10	<10	< 10	<10	< 1	<1
1,1,2,2-Tetrachloroethane			3 - 6	< 0.4	< 10	<10	< 10	<10	< 0.4	<0.4
1,2-Dichloropropane					< 10	<10	< 10	<10		
Cis-1,3-Dichloropropene			< 1	< 0.1-<0.7						
Trans-1,3-Dichloropropene			< 0.7- 2	< 0.7-< 1						
Benzene	>100	<10	<10 -4700	< 0.5-<10	>100	<10	90->100	6	31000	<1
Toluene	>100	<10	<10 -4200	< 1 -<10	>100	<10	>100	35	44000	<1
Ethylbenzene	>100	<10	<10 ->100	< 1 -<40	>100	<10	< 10- 20	<10	< 0.5	<0.5
Acrolein			<10 - 460	< 1 -<10						

[a] The seventeen refineries considered in this study were distributed as follows: Class A - 1; Class B - 7; Class C - 3; Class E - 1; Undesignated Class - 5. The concentration ranges reported for each class are the minima and maxima observed in all the refinery data for the class.

*1 Biotreatment Effluent

*2 Final Effluent

TABLE 43. CONCENTRATION RANGES OF PRIORITY POLLUTANTS - SEMI-VOLATILE EXTRACTABLES CATEGORY REPORTED IN API-EPA PRIORITY POLLUTANTS SURVEY[208]

Parameter (μg/L)	Refinery Category* A		B		C		E		Category Undesignated	
	Bio. Eff.*1	Final Eff.*2	Bio. Eff.*1	Final Eff.*2	Bio. Eff.*1	Final Eff.*2	Bio. Eff.*1	Final Eff.*2	Bio. Eff.*1	Final Eff.*2
Phenol	13	<50	<50 -16000	< 1 - 1.9	3000-8000	<20	40 -1300	< 1	<10 -4900	<0.1-<10
2-Chlorophenol							<50	<50		
2,4-Dimethylphenol			<10 - 3000	< 0.2 - 3.5	< 1	<50	71 -<100	<50	80	2.2
2,4-Dichlorophenol							<50	<50	< 0.1	<0.1
2-Nitrophenol							<50	<50		
4-Nitrophenol							<50	<50		
Pentachlorophenol			<10 - 850	<10			<50	<50		
p-Chloro-m-cresol			<50	<30			10 -< 20	<50		
4,6-Dinitro-o-cresol							<50	<50	< 0.6	<1
N-Nitrosodiphenylamine			<10	<10						
1,4-Dichlorobenzene					< 1	< 1				
1,2-Dichlorobenzene					< 1	< 1				
Dimethyl phthalate			<10	<10					<10	<10
Diethyl phthalate	12	< 1	5.5- 40	< 0.3 - 5			< 1	< 1	<10 - 16	4.3-<10
Di-n-butyl phthalate	1.3	0.7	< 1 - 2.8	2 - 32	< 1	< 1	< 1	< 1	< 0.1-< 10	<1 - 10
Butyl benzyl phthalate							< 1	< 1		
Bis(2-ethyl hexyl) phthalate			< 1 - 600	< 1 - 15			< 1	< 1	< 0.1-1100	<0.1-2000
Naphthalene	68	< 1	< 1 - 1100	< 0.1 - 0.1	106	< 1	27 - 302	< 1	<10 -1100	<0.1-< 10
Acenaphthylene	4	< 1	< 0.1-< 1	< 0.1 -< 1			< 1 - 87	< 1		
Acenaphthene	37	< 1	< 0.1- 3000	< 0.1 - 6	149	< 1	< 1 - 522	< 1		
Fluorene			2.9- 304	< 0.1 - 0.6	106	< 1	< 1	< 1	21	<0.1
Phenanthrene			2.7- 32	< 0.2	< 0.5	< 0.5	0.01- 28	< 0.3		
Anthracene			< 0.01-< 0.03	< 0.01	< 2	< 2	0.1 - 0.2	< 0.02		
Phenanthrene/Anthracene	4.6	< 1	< 1 - 234	< 0.1 - 0.8	48	< 1	0.6 - 126	< 1	<10 -1100	<0.1-< 10
Fluoranthene			< 0.1- 30	< 0.1 -<10	< 1- 8	< 1	< 1 - 7.5	< 1	3.9- 40	<0.1-< 10
Pyrene			< 1 - 20	< 1 - 7	3	< 0.5	0.7 - 16	< 1	5.4	<0.1
Chrysene			0.1- 20	< 0.02- 1.4		< 0.1	< 1 - 5.5	< 1		
Benz(a)anthracene			0.1- 1.4	< 0.02- 0.08			< 1	< 1		
Chrysene/Benz(a) anthracene			0.3- 50	0.1 - 0.8					1.8- 40	<0.1-< 10
Benzo(b)/(k)fluoranthene			< 1	< 1			< 1	< 1		
Benzo(b)fluoranthene							< 0.09- 0.3	< 0.06		
Benzo(k)fluoranthene							< 0.3 - 0.3	< 0.2		
Benzo(a)pyrene			0.1- 9.5	0.1 - 2.9			< 1	< 1		
Indeno(1,2,3-c,d) pyrene			< 1	< 1			< 1	< 1		
Dibenzo(a,h) anthracene			< 0.3	< 0.3			< 1	< 1		
Benzo(g,h,i)perylene			< 0.2- 0.2	< 0.2 - 0.2			< 1	< 1		

*The seventeen refineries considered in this study were distributed as follows: Class A - 1; Class B - 7; Class C - 3; Class E - 1; Undesignated Class - 5. The concentration ranges reported for each class are the minima and maxima observed in all the refinery data for the class.

*1 Biotreatment Effluent

*2 Final Effluent

TABLE 44. CONCENTRATION RANGES OF PRIORITY POLLUTANTS - TOTAL METALS CATEGORY REPORTED IN API-EPA PRIORITY POLLUTANTS SURVEY[208]

Parameter (µg/L)	Refinery Category[a]									
	A		B		C		E		Category Undesignated	
	Bio. Eff.[*1]	Final Eff.[*2]	Bio. Eff.[*1]	Final Eff.[*2]	Bio. Eff.[*1]	Final Eff.[*2]	Bio. Eff.[*1]	Final Eff.[*2]	Bio. Eff.[*1]	Final Eff.[*2]
Ag	< 5	< 5	< 1 - 2	< 1 - 15	< 5	< 5	< 5	< 5	<1 -< 5	<1 -< 5
As	12	<10	< 2 - 41	< 4 - 31	<10 -<20	<10 -<20	<20	<20	<4 - 480	<4 -900
Be	< 3	< 3	< 1 -< 3	< 1 -< 3	< 3	< 3	< 3	< 3	<1 -< 3	<1 -< 3
Cd	< 1	< 1	< 1 - 7	< 1	< 1	< 1	< 1	< 1	<1 - 16	<1 - 5
Cr	32	5	< 5 -3600	< 5 -1000	73 -240	24 -110	650 -1400	120	1 -1600	1 - 73
Cu	17	< 5	2 - 500	< 5 - 125	< 5 - 30	< 5 - 8	13 - 61	11	3 - 280	3 -180
Hg	< 0.5	< 0.5	< 0.1- 6	< 0.1- 6	< 0.5	< 0.5	< 0.5	< 0.5	<0.2- 9	<0.2- 6
Ni	23	<15	< 1 - 77	3 - 58	<15 - 28	<15 - 19	<15 - 16	<15	<1 - 44	<1 - 15
Pb	64	<15	<15 -2000	9 -< 15	<15 - 27	<15	<15 - 18	<15	2 - 430	2 - 58
Se	<10	<10	< 4 - 31	<10 - 27	<10 -<20	12 -<20	<20	<20	<4 - 15	3 - 32
Sb	<25	<25	< 1 - 360	< 1 - 370	<25	<25	<25	<25	1 -< 25	<1 -<25
Tl	<15	<15	< 1 - 3	< 1 -< 15	<15	<15	<15	<15	<1 -< 15	<1 - 12
Zn	220	30	30 -2100	25 - 400	50 -140	<10 - 90	570 -4800	35	24 -1400	36 -700

[a] The seventeen refineries considered in this study were distributed as follows: Class A - 1; Class B - 7; Class C - 3; Class E - 1; Undesignated Class - 5. The concentration ranges reported for each class are the minima and maxima observed in all the refinery data for the class.

[*1] Biotreatment Effluent

[*2] Final Effluent

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TABLE 45. CONCENTRATIONS OF PESTICIDES AND ASBESTOS CATEGORIES OF PRIORITY POLLUTANTS OBSERVED IN DATA OBTAINED DURING API-EPA PRIORITY POLLUTANTS SURVEY[209]

Parameter	Concentration (μg/L)*	Refinery Class	Sample Source
β-BHC	0.7	B	Cooling tower blowdown
Chlordane	2.8	B	Intake water
α-endosulfan	0.1	unknown	DAF effluent
Heptachlor epoxide	4.6	E	Chem. plant effluent
PCB 1221	0.1	B	Cooling tower blowdown
	<5	B	Final effluent
	0.1	E	Separator effluent
PCB 1232	0.9	A	Separator effluent
	3.5	unknown	DAF effluent
	0.5	B	Separator effluent
	0.5	E	Separator effluent
	0.1	E	Chem. plant effluent
PCB 1242	1.1	B	DAF effluent
	0.2	C	DAF effluent
	0.5	unknown	Separator effluent
	0.5	unknown	DAF effluent
	0.5	B	Separator effluent
	0.1	B	Bio-pond influent
	0.2	B	Intake water
	5.2	B	Separator effluent
PCB 1016	1.8	unknown	Separator effluent
	7.9	unknown	DAF effluent
	0.2	B	Separator effluent
	1.9	E	Separator effluent
	1.3	E	Chem. plant effluent
Asbestos	no fibers	unknown	50 ml separator effluent
	no fibers	unknown	50 ml final effluent
	3.4[a]	B	25 ml separator effluent
	no fibers	B	25 ml final effluent
	no fibers	C	50 ml DAF effluent
	no fibers	C	25 ml final effluent
	no fibers	B	50 ml separator effluent
	no fibers	B	100 ml final effluent

[a] Units – millions of fibers per liter

*Concentration (μg/L) except asbestos

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TABLE 46. MEDIAN PERFORMANCE OF ACTIVATED SLUDGE TREATMENT PLANTS FOR THREE CLASS B REFINERIES AND TWO CLASS C REFINERIES[206]

Parameter[a]	Median Influent Concentration	Median Effluent Concentration	Median Treatment Efficiency (% Removal)
BOD_5	85	8.5	89.2
COD	213	70	54.6
TOC	55.5	25	41.9
Oil and Grease	29.2	11	60.0
Phenols	3.4	0.01	99.6
Suspended Solids	36	25	23.8
Dissolved Solids	968	1170	-8.8
Sulfides	2.88	0.275	90.0
Chromium	1.43	0.26	58.2
Ammonia	12.5	11.25	16.2
Organic Nitrogen	3.64	2.9	22.5
Nitrate Nitrogen	0.13	0.055	43.6
Acidity	0	8	0
Alkalinity	139	100	55.1
Phosphate	0.31	0.68	-1.4
Cyanides	0.22	0.1	30.9
Chloride	188.5	175.5	6.6
Iron	1.02	0.78	37.1
Copper	0.14	0.05	57.7
Lead	0.1	0.11	0.0
Zinc	0.22	0.16	22.0
Nitrite	0.1	0.02	27.8
T.K.N.	16.56	14.58	17.2
pH	8.8	7.3	16.5
Conductivity	1475	1450	-5.9
Color	30	30	0
Turbidity	27	18.5	39.2
Volatile Suspended Solids	21	18.5	8.6

[a] All units are mg/L except pH, which is reported in pH units, turbidity, which is reported in J.T.U., and color, which is reported in color units.

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of pollutants observed in this study are presented in Tables 47 through 49.

Furthermore, four of the refineries studied above[209] participated in a pilot-scale PAC study. The study was conducted using a small AC pilot unit to which PAC was added batchwise. The analytical data for pilot plant influents and effluents for traditional and priority pollutants are summarized in Table 50.

A study of 15 case histories of refinery treatment plants achieving levels I and II abatement was made by ES and was summarized in a 1975 report[210]. All available effluent quality data for these treatment plants were analyzed and the long-term average concentrations for the contaminants controlled by effluent guidelines were determined. These data are presented in Table 51. In most cases the data extended over a greater than 12-months time span, so the concentrations reported were considered to be annual averages.

Also as part of the ES report[210], a comprehensive summary was made of data available from the pilot-scale and full-scale applications of AC to refinery and refinery-related wastewaters. These data were tabulated for four wastewater parameters; COD, TOC, oil and grease, and phenols, and are shown in Table 52.

A 1979 EPA indicatory fate study[211] presented data for a number of priority pollutants at several stages of wastewater treatment in a sample refinery. The refinery process wastewater was passed through API separators and DAF units. This clarified wastewater became the influent to the biological treatment system. Biotreatment consisted of two parallel extended aeration basins with clarifiers. One aeration basin contained PAC as part of the mixed liquor, and PAC return sludge and effluent samples were analyzed from this system. The other aeration basin and clarifier was operated without carbon and return sludge and final effluent samples were analyzed. The data from this study are reported in Table 53. In addition, an air-stripper sampler equipped with a resin trap was placed in each aeration basin at a point after the entry of DAF effluent. After a 49-hour operation time with an air flow rate of 300 cfh, the resin traps were removed and analyzed. The results are presented in Table 54.

WASTEWATER RESIDUALS

Wastewater residuals from the petroleum refining industry include sludges produced by chemical and biological means and oily residues. A survey of the literature produced limited data on emissions of specific pollutants from chemical and biological sludges specifically from refineries. Data as to the composition of oily residues were found in a 1972 EPA report[212]. In this report; a study of oily waste disposal by soil cultivation, three simulated oily sludges were investigated. One of the sludges was a crude oil tank bottoms which contained a natural balance of hydrocarbon types; another was a high molecular weight fuel oil (bunker C or No. 6) which contained olefinic and aromatic components; and the third was a waxy raffinate, an intermediate waxy oil product containing highly paraffinic components. The properties of these simulated sludges are summarized in Table 55. Additional data on the oil content of the soil

TABLE 47. CONCENTRATION RANGES OF CLASSICAL PARAMETERS AND THE PRIORITY POLLUTANT TOTAL METALS OBSERVED IN PILOT-SCALE GRANULAR ACTIVATED CARBON TREATMENT OF THREE CLASS B REFINERIES[209]

Parameter[a,b]	Filter Influent	Filter Effluent	Virgin Carbon Effluent	Regenerated Carbon Effluent
BOD_1	< 6 - 27	<6 - 30	<3 -24	2 -14
BOD_3	4 - 23	4 - 23	4 -23	5 - 6
COD	24 -120	20 -160	12 -81	10 -81
TOC	13 - 54	8 - 70	6 -52	3 -70
Total Suspended Solids	4 - 36	1 - 34	2 -11	1 -11
Ammonia Nitrogen	3.9 - 22	2.2 - 22	[illegible]	[illegible]
Cr^{+6}	< 0.02 - 0.02	<0.02 - 0.0	<0.02 - 0.02	<0.02
Sulfides	< 0.1 - 0.5	<0.1 - 0.4	[illegible]	[illegible]
Oil & Grease	4 - 40	4 - 26	[illegible]	[illegible]
pH	7.2 - 7.7	6.8 - 7.9	[illegible]	[illegible]
T. Cyanide	0.01 - 0.12	0.01 - 0.12	[illegible]	[illegible]
Phenols	0.012- 0.090	0.013- 0.09	[illegible]	[illegible]
Hg	< 0.0005	<0.0005	[illegible]	[illegible]
Ag	< 0.001-< 0.005	<0.001-< 0.00	[illegible]	[illegible]
As	< 0.020	<0.020	[illegible]	[illegible]
Be	< 0.001-< 0.003	<0.001-< 0.00	[illegible]	[illegible]
Cd	< 0.001- 0.010	<0.001-< 0.00	[illegible]	[illegible]
Cr (total)	< 0.005- 0.060	<0.005- 0.05	[illegible]	[illegible]
Cu	< 0.005- 0.032	<0.005- 0.01	[illegible]	[illegible]
Ni	< 0.005- 0.016	<0.005- 0.016	[illegible]	[illegible]
Pb	< 0.015- 0.020	<0.015-< 0.020	[illegible]	[illegible]
Sb	< 0.025- 0.470	<0.025- 0.430	[illegible]	[illegible]
Se	< 0.020- 0.062	<0.020- 0.056	[illegible]	[illegible]
Tl	< 0.015	<0.015	[illegible]	[illegible]
Zn	0.015-< 0.060	0.020- 0.070	[illegible]	[illegible]

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[a] All concentrations reported in mg/L except pH which is reported in [illegible]

[b] All analyses for parameters in this listing from BOD_1 through pH we [illegible] under contract to the Effluent Guidelines Division of E.P.A. All c [illegible] T. Cyanide through Zn were performed by the R. S. Kerr Environm [illegible] E.P.A.

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TABLE 48. CONCENTRATION RANGES OF CLASSICAL PARAMETERS AND THE PRIORITY POLLUTANT TOTAL METALS OBSERVED IN PILOT-SCALE GRANULAR ACTIVATED CARBON TREATMENT OF TWO CLASS C REFINERIES[209]

Parameter[a,b]	Filter Influent	Filter Effluent	Virgin Carbon Effluent	Regenerated Carbon Effluent
BOD$_1$	10 –<12	<3 – 30	<3 – 9	<6 –11
BOD$_5$	6 – 13	<5 – 30	3 – 8	3 –10
COD	75 –150	42 –120	10 –88	8 –88
TOC	17 – 55	15 – 53	5 –34	4 –34
Total Suspended Solids	7 – 42	1 – 30	<1 –52	1 –24
Ammonia Nitrogen	<1 – 3.4	<1 – 2.8	<1 – 3.4	<1 –12
Cr^{+6}	<0.02 – 0.02	<0.02 – 0.04	<0.02 – 0.02	<0.02 – 0.02
Sulfides	0.3 – 0.8	0.3 – 0.7	0.1 – 0.7	0.1 – 0.5
Oil & Grease	3 – 30	7 – 17	6 –22	3 –22
pH	7.5 – 8.4	7.6 – 8.6	7.4 – 8.3	7.3 – 8.5
T. Cyanide	<0.02 – 0.10	<0.02 – 0.09	<0.02 – 0.09	<0.02 – 0.09
Phenols	<0.01 – 0.030	<0.012 – 0.040	<0.008 –<0.012	<0.008 –<0.012
Hg	<0.0008 – 0.0008	<0.0008	<0.0008	<0.0008
[illegible]	<0.001 – 0.008	<0.001 – 0.003	<0.001 – 0.010	<0.001 – 0.007
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible] (total)	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Zn	[illegible]	[illegible]	[illegible]	[illegible]

[a] All concentrations reported in mg/l, except pH, which is reported in pH units.

[b] All analyses for parameters in this listing from BOD$_1$ through pH were performed by laboratories under contract to the Effluent Guidelines Division of E.P.A. All analyses for parameters from T. Cyanide through Zn were performed by the R. S. Kerr Environmental Research Laboratory of E.P.A.

TABLE 49. CONCENTRATION RANGES OF CLASSICAL PARAMETERS AND THE PRIORITY POLLUTANT TOTAL METALS OBSERVED IN PILOT-SCALE GRANULAR ACTIVATED CARBON TREATMENT OF A REFINERY OF UNKNOWN CLASSIFICATION[209]

Parameter[a,b]	Filter Influent	Filter Effluent	Virgin Carbon Effluent	Regenerated Carbon Effluent
BOD_1	<6 – <30	<12	<6	<6 – 120
BOD_5	–	–	–	–
COD	96 – 170	52 – 60	1 – 13	15 – 16
TOC	32 – 58	18 – 25	6 – 11	8 – 12
Total Suspended Solids	33 – 66	1 – 7	<1 – 2	<1 – 2
Ammonia Nitrogen	6.2 – 11	5.6 – 11	5.6 – 11	5.6 – 11
Cr^{+6}	<0.02	<0.02	<0.02	<0.02
Sulfides	0.6 – 0.8	0.5	0.2 – 0.6	0.3 – 0.6
Oil & Grease	21 – 42	8 – 8	4 – 9	<1 – 8
pH	7.1 – 7.3	7.1 – 7.4	7.2 – 7.3	7.1 – 7.3
T. Cyanide	<0.02	<0.02	<0.02	<0.02
Phenols	0.018 – 0.031	0.017 – 0.029	<0.01 – <0.013	<0.01 – 0.013
Hg	0.0008	<0.0008	<0.0013	<0.0013
[illegible]	<0.001 – 0.003	<0.001 – <0.003	<0.001 – <0.003	<0.001 – 0.003
[illegible]	<0.020	<0.020	<0.020	<0.020
[illegible]	<0.001 – 0.003	<0.001 – <0.003	<0.001 – <0.003	<0.001 – 0.003
[illegible]	<0.001 – 0.003	<0.001 – <0.003	<0.001 – <0.003	<0.001 – 0.003
[illegible] (total)	0.190 – 0.300	0.030 – 0.040	0.010	0.010 – 0.030
[illegible]	0.005 – 0.030	<0.005 – 0.010	<0.005 – <0.005	<0.005 – 0.005
[illegible]	<0.005 – 0.015	<0.005 – <0.015	<0.005 – <0.015	<0.005 – 0.015
[illegible]	<0.015 – 0.030	<0.015 – <0.030	<0.015 – <0.030	<0.015 – 0.030
[illegible]	<0.025	<0.025	<0.025	<0.025
[illegible]	<0.025	<0.025	<0.025	<0.200
[illegible]	<0.015	<0.015	<0.015	<0.015
[illegible]	0.200 – 0.210	0.185 – 0.190	0.200 – <0.200	0.225 – <0.260

[a] [illegible]

[b] [illegible]

TABLE 30. CONCENTRATION RANGES OF CLASSICAL PARAMETERS AND THE PRIORITY POLLUTANT TOTAL METALS OBSERVED IN PILOT-SCALE POWDERED ACTIVATED CARBON TREATMENT OF REFINERY WASTEWATERS[209]

Parameter[a,b]	Refinery Class[c] B Pilot Plant Influent	B Pilot Plant Effluent	C Pilot Plant Influent	C Pilot Plant Effluent	Class Undesignated Pilot Plant Influent	Class Undesignated Pilot Plant Effluent
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	<60 - 110	<6 -<12
[illegible]	[illegible]	[illegible]	-	-	-	-
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	480 -1400	36 - 76
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	110 - 450	12 - 29
Total Suspended Solids	[illegible]	[illegible]	[illegible]	[illegible]	150 - 860	6 - 30
Ammonia Nitrogen	[illegible]	[illegible]	[illegible]	[illegible]	5.6 - 10	2.0 - 3.4
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.02 - 0.11	<0.02
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.8 - 2.7	0.6 - 0.7
Oil & Grease	[illegible]	[illegible]	[illegible]	[illegible]	98 - 470	10 - 13
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	7.1 - 7.4	7.5 - 7.7
Cyanide	[illegible]	[illegible]	[illegible]	[illegible]	0.01 - 0.02	<0.02
Phenols	[illegible]	[illegible]	[illegible]	[illegible]	0.23 - 3.6	<0.012- 0.014
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	<0.0005	0.0006
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	<0.001-< 0.005	<0.001-< 0.005
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	<0.020	<0.020
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.002-< 0.003	<0.001-< 0.003
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	<0.002- 0.003	<0.001-< 0.002
[illegible] (total)	[illegible]	[illegible]	[illegible]	[illegible]	1.700- 2.000	0.049- 0.070
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.370- 0.400	0.008- 0.020
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.020- 0.027	<0.005-< 0.015
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.060- 0.100	<0.015-< 0.020
[illegible]	[illegible]	[illegible]	[illegible]		<0.025	<0.025
[illegible]	[illegible]	[illegible]	[illegible]		<0.020	<0.020
[illegible]	[illegible]	[illegible]	[illegible]		<0.015	<0.015
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.800- 10.000	6.105- 0.120

[a] All concentrations reported in mg/l except pH, which is reported in pH units.

[b] All analyses for parameters in this listing from BOD5 through pH were performed by laboratories under contract to the Effluent Guidelines Division of E.P.A. All analyses for parameters from 1, Cyanide through Zn were performed by the R. S. Kerr Environmental Research Laboratory of E.P.A.

[c] Four refineries comprised this part of the study - 2 Class B, 1 Class C, and 1 Undesignated Class.

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TABLE 51. CASE HISTORY LONG-TERM EFFLUENT CONCENTRATIONS FOR PLANTS CONFORMING TO ABATEMENT LEVELS I AND II[210]

Case Number	Subcategory	Throughput Capacity (1,000 b/sd)	Treatment System	Annual Average Concentrations in mg/L								
				BOD	COD	TSS	Oil and Grease	Phenol	NH_3-N	Sulfide	Total Cr	Cr^{+6}
Level I Systems												
1	C	60	AS[a]	13	174	78	9.4	0.050	1.10	0.27	0.41	-
2	C	63	AS	16	130	30	9.0	0.15	6.7	0	1.35	-
3	B	135	AS	18	132	23	-	-	-	-	-	-
4	B	63	AS	28	183	41	-	-	-	-	-	-
5	B	205	AS	12	112	15	9.9	0.04	8.2	0	-	-
6	D	293	TF[b]+AS	18	121	19	-	-	-	-	-	-
7	B	160	AS+PP[c]	-	87	7	-	-	13.7	-	-	-
8	D	175	AL[d]+PP	-	68	28	5.1	0.04	28	-	-	-
9	D	331.6	AL	36	-	47	35	0.43	3.9	-	-	-
10	B	63	AL+PP	21	187	24	-	-	-	-	-	-
11	C	85	AL+PP	10	148	20	-	-	-	-	-	-
12	D	331.6	AL+DAF[e]	15	-	15	5	0.35	3.8	-	-	-
14	C	53	AL	25	-	58	13	0.80	54	1.3	-	-
15	C	95	AS+PP	24	142	41	-	-	-	-	-	-
Level II Systems												
13	B	205	AS+MMF[f]	11	104	13	8.6	0.05	3.4	0	-	0.12
14	C	53	AL+MMF	16	-	27	7.8	0.47	53	0.9	-	-

[a] AS - Activated Sludge
[b] TF - Trickling Filter
[c] PP - Polishing Pond
[d] AL - Aerated Lagoon
[e] DAF - Dissolved Air Flotation
[f] MMF - Mixed Media Filtration

TABLE 52. CASE HISTORY ACTIVATED CARBON APPLICATIONS IN PETROLEUM REFINERY WASTEWATER TREATMENT[210]

Case	Description	Capacity	COD (mg/L) Range	COD (mg/L) Average	Avg. % Rem.	TOC (mg/L) Range	TOC (mg/L) Average	Avg. % Rem.	Oil & Grease (mg/L) Range	Oil & Grease (mg/L) Average	Avg. % Rem.	Phenols (mg/L) Range	Phenols (mg/L) Average	Avg. % Rem.
1	Activated Sludge Effluent Sand Filter 3" ϕ Pilot Plant	$0.05 \text{ to } 0.07 \frac{\text{lb COD}}{\text{lb C}}$	4- 55	27	55	11-28	17	50						
2	API Separator Effluent Sand Filter 5" ϕ Pilot Plant	$0.05 \text{ to } 0.6 \frac{\text{lb COD}}{\text{lb C}}$	75-310	197	63									
3	API Separator Effluent Sand Filter 5" ϕ Pilot Plant	$0.23 \frac{\text{lb TOC}}{\text{lb C}}$ $0.3 \frac{\text{lb BOD}}{\text{lb C}}$ $(0.6 \frac{\text{lb COD}}{\text{lb C}})^*$	-	-	-	10-16	13	65	0.8-2.4	1.8	86	<.001-.007	0.023	99
4	Full Scale System	$0.12 \frac{\text{lb TOC}}{\text{lb C}}$	24-915	252	32	-	-	-	<1 -61	7.4	76	<1 -47	9.2	30
5	API Separator Effluent Stabilization Pond Effluent Sand Filter 6" ϕ Pilot Plant	$0.46 \text{ to } 0.73 \frac{\text{lb COD}}{\text{lb C}}^*$				2-21 2-15	6 11	81 64	<1 -16 <1 -2	1.7 0.9	97 94	0.01-0.02 0.01-0.07	0.01 0.015	99+ 99+
6	Pilot Plant	$0.1 \text{ to } 0.6 \frac{\text{lb COD}}{\text{lb C}}$ $0.1 \frac{\text{lb BOD}_5}{\text{lb C}}$	50- 75	60	64									
7	API Separator Effluent Biological Effluent Sand Filter 5" ϕ Pilot Plant	$1.2 \frac{\text{lb COD}}{\text{lb C}}^*$ $0.25 \frac{\text{lb COD}}{\text{lb C}}^*$	- -	103 26	55 73	- -	14 7	75 76	- -	10 7	65 30	- -	0.004 0.001	99+ 90
8	4" ϕ Pilot Plant Aqueous Saturated Mixture of Naphthas and Heavy Condensate Oils	$0.2 \text{ to } 0.3 \frac{\text{lb COD}}{\text{lb C}}$ $0.09 \text{ to } 0.15 \frac{\text{lb TOC}}{\text{lb C}}$					<15	90+						
9	DAF Effluent Pilot Plant Columns	-	<10-100	29	78	35-65	47	39	0 -6	1.9	59	0 -0.25	0.035	99+
10	Full-Scale Treatment of Storm Runoff and Process Waters from Refinery	$0.15 \text{ to } 0.39 \frac{\text{lb COD}}{\text{lb C}}$ $0.21 \frac{\text{lb COD}}{\text{lb C}}$												
	a. Single-Stage Treatment		15-158	53	79									
	b. Two-Stage Treatment		8-105	47										

*Estimated Values

(continued)

TABLE 52 continued

Case	Description	Capacity	COD (mg/L) Range	COD (mg/L) Average	Avg. % Rem.	TOC (mg/L) Range	TOC (mg/L) Average	Avg. % Rem.	Oil & Grease (mg/L) Range	Oil & Grease (mg/L) Average	Avg. % Rem.	Phenols (mg/L) Range	Phenols (mg/L) Average	Avg. % Rem.
11	Pilot Plant	0.16 $\frac{\text{lb COD}}{\text{lb C}}$	48-170	109	60	14-49	29	67						
	DAF Effluent													
	Act. Sludge Effluent													
	Oxidation Pond Effluent													
	Lime Clarifier Effluent													
	4-3" ϕ Carbon Columns													
12	Pilot Plant		79 max.	41	57							0.095 max.	0.03	96
	Rotating Disks													
	Sand Filter													
	5 Carbon Columns													
13	API Separator Effluent													
	Air Flotation - 6" ϕ Col.					2-17	-	<20						
	Chemical Coagulation - 2" ϕ Col.					2-14	-	<20						
	Filtration - 2" & 6" ϕ Cols.					3-22	-	<20						

TABLE 53. ANALYTICAL DATA FOR PRIORITY POLLUTANTS FROM ONE REFINERY[211]

Parameter	Influent (μg/l)	PAC Return Sludge (μg/l)	Return Sludge (μg/l)	PAC Effluent (μg/l)	Final Effluent (μg/l)
CLASSICAL					
TOTAL CYANIDES (mg/L)*	< .05	< .05	< .05	< .05	< .05
TOTAL PHENOL	417	386	67	42	29
TOTAL METALS					
Arsenic	<10	260	150	<10	<10
Selenium	<10	400	280	<10	<10
Cadmium	< 1	31	24	< 1	< 1
Beryllium	< 3	20	9	< 3	< 3
Copper	45	5,800	4,900	18	16
Antimony	<10	< 10	< 10	<10	<10
Chromium	280	64,000	60,000	100	72
Nickel	17	1,200	1,100	14	17
Zinc	390	37,000	28,000	140	130
Silver	<10	22	22	<10	<10
Thallium	<10	< 10	< 10	<10	<10
Lead	40	12,000	11,000	18	14
Mercury	< 0.6	< 10	< 10	< 1.0	≤ 0.8
ORGANICS (GAS CHROMATOGRAPHY)					
PURGEABLES					
Methylene chloride	<10	NA	NA	<10	<10
Chloroform	<10	NA	NA	<10	<10
Benzene	320	NA	NA	<40	<40
1,1,2,2-Tetrachloroethylene	<10	NA	NA	<10	<10
Toluene	695	NA	NA	<10	<10
Ethylbenzene	56	NA	NA	<10	<10
POLYNUCLEAR AROMATICS					
Pyrene	<10	< 12	< 13	<10	<10
Benzo-a-pyrene	<44	< 106	< 110	<13	<11
Chrysene	<10	< 14	< 14	<10	<10
Fluoranthrene	<10	< 12	< 13	<10	<10
Phenanthrene/Anthracene	<10/<10	<14/<16	<14/<17	<10/<10	<10/<10
Naphthalene	282	< 14	< 14	<10	<10
Acenaphthene	24	< 10	< 10	<10	<10
Fluorene	<16	< 39	< 41	<10	<10
PHENOLS					
2,4-Dimethylphenol	142	10	ND	ND	ND
PHTHALATE ESTERS					
Dimethyl phthalate	<10	< 10	< 10	<10	<10
Diethyl phthalate	<10	< 10	< 10	<10	<10
Di-n-butyl phthalate	<10	< 10	< 10	<10	<10
Bis-(2-ethylhexyl) phthalate	<16	< 16	< 19	<16	<19

*Note: Total Cyanides expressed in mg/L.

NA - Not Applicable
ND - Not Detectable, or less than detectable limits

TABLE 54. AIR-STRIPPER SAMPLER ANALYSIS RESULTS FROM ONE REFINERY[211]

Priority Pollutant	Sparged Air, XAD-2 Resin (µg)	
	PAC	Control
POLYNUCLEAR AROMATICS		
Naphthalene	ND	ND
2-Chloronaphthane	30	220
Acenaphthalene	<10	<10
Acenaphthene	<10	<10
Fluorene	<13	<13
Phenanthrene/Anthracene	<10	<10
Fluoranthene	<10	<10
Pyrene	<10	<10
1,2-Benzanthracene	20	<10
Chrysene	20	<10
3,4-Benzopyrene	<35	<35
1,2:5,6-Dibenzanthracene	ND	ND
PHENOLICS		
2-Chlorophenol	<25	<25
2-Nitrophenol	<25	<25
Phenol	<10	<10
2,4-Dimethylphenol	<25	<25
2,4-Dichlorophenol	<50	<50
2,4,6-Trichlorophenol	<10	200
4-Chloro-m-cresol	80	30
2,4-Dinitrophenol	<100	<100
4,6-Dinitro-o-cresol	<25	<25
Pentachlorophenol	<25	<25
4-Nitrophenol	<25	<25

ND - Not Detectable, or less than detectable limits.

TABLE 55. PROPERTIES OF SIMULATED OILY SLUDGES USED IN STUDY OF DISPOSAL BY SOIL CULTIVATION[212]

		SLUDGE		
Parameter	Tank Bottoms	Crude Oil	Bunker C	Waxy Product
Spec. Grav., 60/60°F		0.86	1.03	0.85
Lbs/Gal		7.12	8.57	7.08
Pour Point, °F		-5	40	95
Viscosity, SU, 60°F		60	19,000	-
,SSF, 122°F		-	120	59
Hydrocarbon Type, %w				
Saturate		36	18	90
Resins		8	26	-
Aromatic		56	56	10
Total Sulfur, %w		0.47	1.96	0.04
Total Nitrogen, %w		0.09	0.41	<0.0005
Total Phosphorus, PPM		6	11	5
Total Ash, PPM	31,000		320	8
Calcium	1,880		10	Nil
Magnesium	375		1	Nil
Sodium	3,135		15	Nil
Iron	1,255		20	Nil
Copper	94		1	Nil
Lead	Nil		Nil	-

samples, chronological data, penetration depths, hydrocarbon types, and microbial profiles are also presented in the EPA report[212].

In the EPA indicatory fate study described previously[211], samples of return sludges from both the conventional and PAC systems, as well as influents and effluents were analyzed. These data are contained in Table 53.

ANALYTICAL CONSIDERATIONS

Wastewater and wastewater residual samples generated by the petroleum refining industry are routinely analyzed by standard techniques. The analytical methods are summarized in several of the reports considered in this study[206,207,208,213] and will not be reiterated here.

However, the topics of accuracy, precision, and variance in refinery waste analysis deserve consideration. Accuracy is a measure of how close analytical results are to the "true" value, while precision is a measure of the repeatability of the analytical results. Precision data are usually easy to obtain, while accuracy data are often difficult or impossible to obtain. Most accuracy measurements are based on a "spiked" sample, in which a known concentration of a parameter to be determined is added to the wastewater sample under consideration, and the "recovery" of the spike is determined[210]. A summary of precision and accuracy data for refinery wastewater analysis is presented in Table 56, and further results on metals are shown in Table 57.

There are a number of reasons that analytical variability and errors exist. Several contributing factors are as follows:

1. Repeatability of the test method itself[208].
2. Interferences from contamination of samples[208], either in field or laboratory.
3. Presence of interfering compounds as part of the wastewater[208].
4. Variability which inevitably exists among laboratories using the same test methods[208].
5. Use of different analytical procedures[208].
6. Interlaboratory analysis of parallel, not true duplicate, samples[208].
7. Inability to perfectly preserve samples for transport from field to laboratory and time delays due to transport[205].

Most of the traditional parameters, such as COD, TOC, oil and grease, and TSS, are analyzable to a reasonably high degree of accuracy, since they routinely exist at levels significantly above the lower detection limit in wastewaters. Biological

TABLE 56. ANALYTICAL VARIABILITY OF WASTEWATER PARAMETERS

Parameter	Test Concentration or Range (mg/L)	Standard Deviation (mg/L)	Spike Recovery (%)	Reference
BOD	175	26		Eng-Sci, Inc. (1975)
COD	12.3	4.15		"
	137.3	13.3	95.1	Myers, et al. (1976)
	270	17.8		Eng-Sci, Inc. (1975)
TOC			101	Myers, et al. (1972)
Oil & Grease - Hexane	11.2	3.5		Myers, et al. (1976)
- Freon	11.1	1.7		"
-Freon with Infrared analysis	13.86	1.4		Eng-Sci, Inc. (1975)
-Freon by separatory funnel	13.0	0.9		"
-Freon by Soxhlet extraction	12.3	1.1		"
Phenol			98	Myers, et al. (1972)
	0.120		42	A.P.I. (1978)
	0.330		45	"
	0.330		42	"
	0.0085		68	"
	0.029		55	"
Phenolics	0.004 -0.009		68-92	"
	0.014 -0.029		55-93	"
	0.084 -0.330		25-89	"
	5.5637	0.6504		Myers, et al. (1976)
-By extraction	0.0096	0.00099		Eng-Sci, Inc. (1975)
	0.0483	0.0031		"
	0.0935	0.0042		"
-By direct photometric analysis	4.7	0.18		"
	48.2	0.48		"
	97.0	1.58		"
Total Suspended Solids	18.6	4.3		Myers, et al. (1976)
Sulfides			85	Myers, et al. (1972)
Chromium	0.353 (0.370)[a]	0.105		Eng-Sci, Inc. (1975)
	0.380 (0.407)	0.128		"
	0.072 (0.074)	0.029		"
	0.084 (0.093)	0.035		"
	0.0102 (0.0074)	0.0078		"
	0.016 (0.015)	0.009		"
Ammonia Nitrogen	8.6	0.7	95.6	Myers, et al. (1976)
-By distillation	0.21	0.122		Eng-Sci, Inc. (1975)
	0.26	0.07		"
	1.71	0.24		"
	1.92	0.28		"
-By specific ion electrode	1.00	0.04		"
	0.77	0.17		"
	0.19	0.007		"
	0.13	0.003		"
-By automated analysis	0.43 -1.41	0.005		"
T.K.N.			100	Myers, et al. (1972)
Nitrate Nitrogen			101	"
Nitrite Nitrogen			101	"

---

[a] True concentration in "spiked" synthetic sample

(continued)

TABLE 56 continued

Parameter	Test Concentration or Range (mg/L)	Standard Deviation (mg/L)	Spike Recovery (%)	Reference
Cyanide			98	Myers, et al. (1972)
	0.06	0.005		Eng-Sci, Inc. (1975)
	0.13	0.007		"
	0.28	0.031		"
	0.62	0.094		"
Cadmium	0.070 (0.071)	0.021		"
	0.074 (0.078)	0.018		"
	0.0168 (0.014)	0.011		"
	0.0183 (0.018)	0.010		"
	0.0033 (0.0014)	0.005		"
	0.0029 (0.0028)	0.003		"
PNA's	0.005 -0.007		46-70	A.P.I. (1978)
	0.018 -0.033		67-84	"
	0.054 -0.220		19-112	"
Phthalate Esters	0.006 -0.025		4-7	"
	0.140 -0.610		41-420	"
Naphthalene	0.074		26	"
	0.210		81	"
	0.210		100	"
	0.0046		46	"
	0.018		67	"
Fluorene	0.054		94	"
	0.160		106	"
	0.160		110	"
	0.0051		49	"
	0.019		84	"
Phenanthrene/anthracene[b]	0.078		113	"
	0.220		104	"
	0.220		91	"
	0.005		70	"
	0.020		75	"
Pyrene	0.033		73	"
	0.095		79	"
	0.095		116	"
	0.0073		48	"
	0.023		70	"
Di-n-butyl phthalate	0.140		300	"
	0.380		25	"
	0.380		55	"
Bis (2-Ethylhexyl) phthalate	0.220		88	"
	0.610		89	"
	0.610		77	"
2-Chlorophenol	0.084		90	"
	0.240		67	"
	0.240		41	"
	0.0036		92	"
	0.014		93	"
Butyl benzyl phthalate	0.0062		6.5	"
	0.025		4	"

[b] The spike compound was phenanthrene.

TABLE 57. ANALYTICAL VARIABILITY OF METAL CONCENTRATIONS IN REFINERY WASTEWATERS[208]

Element	Refinery #1				Refinery #2				Refinery #3			
	Concentration, ng/g			Percent Recovery	Concentration, ng/g			Percent Recovery	Concentration, ng/g			Percent Recovery
	Initial	Spike	Found		Initial	Spike	Found		Initial	Spike	Found	
Zinc	55	100	250	161	82	500	720	124	27	250	280	101
Chromium	110	40	150	100	46	50	140	146	94	100	190	98
Copper	130	33	170	104	16	100	130	112	52	100	130	86
Lead	6.6	5.0	21	181	5.3	5.0	18	175	3	100	63	61
Beryllium	0.2	1.7	1.9	100	0.7	2.0	3.5	130	< .1	1	.7	70
Antimony	5.3	10	20	131	68	100	220	131	36	50	36	42
Thallium	4.8	50	32	58	9.5	50	75	126	< 2	100	48	48
Nickel	3.4	10	13	97	3.6	10	14	103	2.1	25	21	77
Arsenic	22	50	84	117	16	50	62	94	14	100	120	105
Selenium	11	5	15	94	15	50	30	46	74	100	130	75
Silver	1.3	1.7	5.8	193	0.8	2.0	3.0	107	4.2	5	9	98
Cadmium	1.1	2.0	3.3	106	0.8	2.0	3.0	107	1.1	10	12.6	114
Mercury	0.5	0.05	0.5	91	0.4	0.05	0.5	111	0.8	5	2	34

analyses such as BOD are limited in accuracy by the variability of microorganism behavior.

Among the priority pollutants analytical accuracy and precision problems arise from several causes. Many priority pollutant metals are present at quite low concentrations, often very near or below the lower quantifiable level, and often below the limit of detection. As a general rule, the nearer to the limit of detection an analytical result is, the larger the percent error in its determination. Hence many of the metals analyses presented may be reported accurately only by indicating a concentration less than a lower quantifiable level.

Organic priority pollutant analyses are subject to the same errors described above, and others due to the method of analysis. The preferred analytical technique for these tests is analysis by a GC coupled to a MS. In addition to problems of contamination, low-level analysis inaccuracies, and differing procedures of analysis[208], several problems due to the nature of the analytical method arise as summarized below[207]:

1. Obtaining standard samples of the priority pollutant compounds is often a problem.
2. GC-MS data are only semiquantitative at best.
3. MS and data system quadrupole peak errors exist.
4. Low concentration samples can be "lost" in the chromatography column.
5. Efficiency of extraction of the organics from the aqueous phase to an organic solvent phase is variable.
6. Variations in injection volume and technique occur.
7. On many systems there is a loss during the purge step.
8. Inaccuracies arise in dilution and concentration steps.

Despite these limitations, GC-MS analysis provides the most sensitive and most accurate method widely available for determining organic priority pollutants.

Another type of variability arises in the analysis of similar but not identical or duplicate wastewaters. This is the variability which exists in wastewater samples taken from one location at different times, defined by some authors as inherent variability[210]. Several factors influence inherent variability, including the following:

1. Raw waste loading variations;
2. Temperature variations;

3. Dissolved solids variations;

4. pH variations;

5. Nutrient level variations;

6. Dissolved oxygen level variations; and

7. Toxic and/or inhibitory species variations.

Furthermore, obtaining a "representative" sample may involve variabilities. For wastewaters a representative sample may be obtained by continuously withdrawing a small fraction of a waste stream and compositing. A less accurate representative sampling technique, but one often used, is the collection of "grab" samples over specified time intervals and compositing. For sampling solid wastes such as sludges, obtaining a representative sample is quite difficult, and special sampling procedures are often called for in these cases[214].

A detailed discussion of analytical variability of five wastewater parameters in the refining industry is provided in an EPA report published in 1976[213].

ADDITIONAL INFORMATION AVAILABILITY

Since the purpose of this section is to summarize the available data on refinery wastewater pollutant loadings, not all the available data are appropriate for inclusion herein. In this section a brief description of other available information will be provided.

First, in this section little has been said about the volumes of wastewaters emitted by refinery operations. Details of the volumes produced by various operations are presented in reference 209.

Second, data are available concerning the waste loading to a treatment facility caused by once-through cooling water, and a comparison is made to these operations without once-through cooling water. These data are tabulated in reference 206. Also, data on raw waste loadings by desalter brines are presented in reference 210.

Long term expected effluent loadings for a number of treatment technologies are discussed in reference 210. Multimedia environmental goals - for air, water, and solids - are considered from the standpoint of health effects and ecology effects in reference 215. These goals are outlined for over 650 pollutants.

Information on the frequency with which the priority pollutants are used as raw materials, intermediate materials, or are the products of manufacturing processes is presented in reference 209.

The amounts of solid wastes generated by refineries are reported in reference 210. The expected levels of a number of metals in sludges from refineries and other manufacturing and processing operations are given in reference 214.

Further information on analytical variability is also available. Data comparisons of intralaboratory and interlaboratory results are shown in reference 213 for five wastewater parameters, and variability in PNA analysis is discussed in reference 208. Compounds which caused contamination of blanks are listed also in reference 208.

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SECTION 9

RECOMMENDED RESEARCH NEEDS

INTRODUCTION AND PURPOSE

The amount and composition of wastewaters and sludges generated by petroleum refineries are highly variable in nature and are dependent upon a complex matrix of factors which include[216]:

- o The types of refineries and their product slates.
- o Composition of the feedstock crude oils which, in turn, depends upon the geographic sources of the crude oils.
- o The processes and technologies used in the refineries.
- o The geographic location of the refineries and the prevailing climate patterns at those locations.
- o The type of cooling water systems used in the refineries, and whether or not the refineries must handle tanker ballast waters.
- o The degree of air-cooling and wastewater reuse utilized within the refineries.
- o The physical age of the refineries and the degree of good housekeeping practiced within the refineries.

There is a large body of literature and data concerning the characteristics and variability of refinery wastewaters and sludges[216,217]. There is also a large body of literature, data case histories concerning the existing control technologies for the treatment of refinery wastewaters and sludges[218]. The purpose of this section is to delineate and to discuss key areas in which the existing body of literature and data needs to be improved by more research and development so as to provide:

- o More comprehensive, more valid and better correlated data on the amount, composition and variability of refinery wastewaters and sludges.
- o More information related to the long-term toxicity effects of refinery wastewaters upon fish.
- o Better demonstrated and documented data on the design parameters, economics and performance capabilities of existing and emerging control technologies for the treatment of refinery wastewaters and sludges.
- o More and better guidance as to the technological and economic feasibility of methods proposed for the ultimate disposal and/or reuse of treated wastewaters, concentrated pollutant brines and residual sludges.

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Rather than dealing with generalized areas or categories of research, this section focuses upon a number of specific research needs and discusses each specific need on an individual basis.

IDENTIFYING THE SPECIFIC REFINERY WASTEWATER POLLUTANTS WHICH ARE TOXIC TO FISH ON LONG-TERM EXPOSURE

As discussed by Burks[219], short-term (96-hour) fish bioassay tests of the wastewaters from a number of refineries clearly indicate that the effluents from properly operated biotreaters consistently had a mean annual TL_m of greater than 100 percent, which means that more than half of the test fish could survive in the undiluted effluents. On the other hand, wastewaters from refineries without any biotreating had a mean annual TL_m of 19-21 percent, which means that more than half of the test fish could not survive unless the effluents were diluted about 4-to-1. In other words, biotreating of refinery wastewaters consistently removed or degraded those pollutants which are lethal to fish on a short-term (96-hour) exposure.

However, other tests[219] have shown that biotreated refinery wastewaters retain some pollutants which are lethal to fish on a long-term (16-32 day) exposure. There may also be some long-term, sub-lethal effects such as the impairment of spawning activities, or the impairment of the ability to escape predators or to pursue food.

It is not known if the long-term toxicity of biotreated refinery wastewaters is due to low residual levels of the short-term lethal pollutants (which are largely removed by biotreatment) or is due to a completely different group of pollutants. It should be of considerable usefulness to both industry and to regulatory agencies to undertake research studies directed toward:

- o Identifying the specific pollutants retained in biotreated refinery wastewaters which are toxic to fish on a long-term exposure basis.
- o Determining the concentration levels at which the specific effluents exhibit long-term toxicity.
- o Determining the interaction effects (if any) in mixtures of the specific pollutants, which either increase or decrease the long-term toxicity of the individual pollutants.

At a lower level of priority, it is recommended that research also be undertaken to develop techniques for the more rapid determination of long-term toxicity effects. In other words, the development of a technique which could correlate the short-term responses of aquatic organisms with long-term toxicity effects (either lethal or sub-lethal) would be of great value as a research tool as well as a practical effluent monitoring tool. One such biological monitoring technique, based on fish ventilatory responses (breathing behavior), is already under development for use as an on-line, continuous and automated system[220].

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VARIABILITY OF TREATED EFFLUENT QUALITY

Ford[218] presents a comprehensive discussion of the problems associated with the variability of treated effluent quality resulting from process performance variability. The variability in process performance of wastewater treating is dependent upon a multitude of factors, including:

- The inherent variability of biological treatment processes attributable to the basic nature of the process, the influent waste load characteristics, the geographic and climatic conditions prevailing at the plant site, and the sensitivity of biological treatment to seasonal changes in ambient temperatures.
- Changes in raw wastewater flow and composition due to changes in the refinery's feedstock crude oil.
- Changes in raw wastewater flow and composition resulting from events such as maintenance turnarounds, short-term production of specialty products, seasonal changes in product slates, seasonal changes in rainfall, etc.

To some extent, the impacts of the above variability factors may be minimized by installing appropriate surge and equalization ponds, but their impacts cannot be completely mitigated.

Snider and Manning[217] summarize the many factors involved in the variability of analytical test methods for determining pollutant levels in wastewaters. Bomberger[221] discusses the specific problems and inadequacies encountered in the analytical determination of pollutants in refinery sour wastewaters. Burks[219] also reviews some inadequacies in the methods for analyzing organic pollutants in refinery wastewaters.

Both process performance variability and analytical test method variability contribute to the overall problem of treated effluent quality variability. It is recommended that research be undertaken to: (1) determine how much analytical test method variability contributes to overall effluent quality variability, (2) determine which test methods are the least reliable, and (3) develop new, more reliable test methods if possible.

ACTIVATED SLUDGE BIOTREATMENT

There is a most extensive literature base on the theory and design of AC biotreatment of wastewaters. The majority of that literature concerns the theoretical aspects of the biochemical reaction process, such as: reaction kinetics, cellular energy and material balances, sludge yields and sludge characteristics, volatile and non-volatile suspended solids levels in the mixed liquor, food-to-microorganisms ratios, methods of supplying oxygen to the reaction, etc. Such studies have contributed a great deal to our understanding of the theoretical mechanisms of AS biotreatment, but have done little to improve the basic process performance. In fact, Schaumberg and Marsh have pointed out in a JWPCF editorial[222]:

- The number of technical studies concerning activated sludge biotreatment published in the JWPCF over the past 65 years has risen from about 0-25 per year (during the period 1910-1965) to about 145 per year in 1975.
- Yet, the BOD removal efficiency of the activated sludge process has remained constant over the past 65 years (at a level of about 88-96 percent).

It would appear that all of the years of research directed at understanding the process have not improved the process performance beyond that which had been achieved in the early 1900's. It would also appear that there may be merit in re-directing AS research towards correlating key design parameters with process performance instead of further studying of theoretical mechanisms. For example, instead of studying reaction models based upon assuming completely mixed reaction systems, research should be directed toward defining how much mixer horsepower is needed to achieve complete mixing in real-world biotreatment systems. As another example, instead of continuing to study reaction kinetics in glassware systems, there should be more benefit to be derived from correlating reaction basin retention time with process performance in real-world, full-scale biotreaters operating at various parametric levels of mixing horsepower input.

There can be little doubt that improving the performance capabilities of the AS biotreatment process would be most desirable. It is recommended that studies be undertaken to correlate key design parameters, such as mixer horsepower and reaction basin retention time, with actual process performance in the full-scale AS units currently operating in refineries.

GRANULAR ACTIVATED CARBON AS END-OF-PIPE TECHNOLOGY

GAC systems following a biotreater as an end-of-pipe technology is one of the options considered by the EPA as the regulatory basis for their latest BAT effluent limitations for petroleum refineries[223]. The EPA's latest Development Document[223] concerning refinery effluent limitations presents pilot plant test data on the performance of GAC in treating refinery wastewaters. However, the fact remains that only two major refineries have ever installed full-scale GAC systems and operated them on a long-term basis. One of those two systems was intended only for use in treating impounded storm water for a small part of the year. The other system was used as the main treatment process in that there was no biotreater ahead of the AC system. The latter system was eventually shut down because of poor performance.

If GAC systems are to be considered as viable options in arriving at BAT or any other regulatory effluent limitations for refineries, then it would appear that there is a real need for the long-term testing of such systems on a demonstration-scale basis. It is recommended that research grants be used to fund the demonstration of GAC units in petroleum refineries, in sizes capable of treating at least 200-400 gpm of biotreated wastewaters and including the facilities for the necessary carbon regeneration.

ENHANCEMENT OF ACTIVATED SLUDGE BIOTREATMENT BY PAC

The direct addition of PAC has been shown to be a very cost-effective method of enhancing the performance of AS biotreatment of refinery wastewaters[223,224], if it is necessary to achieve an effluent quality better than that which can be achieved by conventional AS processes. Oil industry studies by Sun Oil Company, Amoco and Exxon have provided an extensive amount of data on the PAC enhancement of AS biotreaters. However, the development of an economic method of recovering and regenerating the spent PAC would be a major improvement to the process in terms of cost-effectiveness. Research directed toward that end should be worthy of consideration.

EFFLUENT TREATING VIA CHEMICAL OXIDATION

A number of small refineries utilize chemical oxidation of their wastewater effluents by the addition of hydrogen peroxide or chlorine. Ozonation may also be effective for oxidation. Very little data is available in the literature regarding such applications. A research study aimed at collecting, correlating and publishing actual case history data on the chemical oxidation of refinery wastewaters should be most useful.

LANDFARMING OF WASTEWATER SLUDGES

Landfarming of organic, biodegradable sludges derived from refinery wastewater treatment is an environmentally sound practice when careful consideration is given to site location, soils, hydrology and surrounding land uses in order to minimize the adverse impacts that might arise[218]. Landfarming application rates appear to range from 100-120 barrels of sludge per acre per application with about eight applications per year (allowing four winter months per year when applications are not advisable). Thus, it is possible to landfarm about 800-960 barrels of sludge per acre per year. A good many refineries have tested and practiced landfarming for disposal of oily sludges[225].

There are two areas of research concerning the landfarming of oily sludges which merit consideration:

1. The relationship between oily sludge vapor pressure and problems of odor control and air emissions, if any, and the methods for mitigating such problems (by sub-surface injection, for example).
2. The problems associated with landfarming vis-a-vis RCRA regulations and the methods of resolving any such problems.

ULTIMATE DISPOSAL OF CONCENTRATED POLLUTANT BRINES AND FEASIBILITY OF METHODS PROPOSED FOR "ZERO DISCHARGE"

Technologies such as reverse osmosis and vapor compression evaporation do exist which may be technically feasible for the concentration and desalination of treated wastewaters from refineries, although such technologies have not yet been practiced on a large scale in the refining industry. Such technologies are very costly and energy-intensive, and their endproduct is essentially a concentrated pollutant brine. The ultimate disposal of such brines in an environmentally sound and secure method which prevents their dissolution by subsequent rainfall poses a very difficult problem. Transport of pollutant brines to some disposal site merely transfers the problem without providing an ultimate resolution of the problem.

Injection of concentrated brines, or residual wastewaters, into underground disposal wells may be environmentally acceptable in those locations where the sub-surface geology and hydrology are deemed suitable for such disposal.

Evaporation-percolation ponds are listed in the EPA's Development Document[223] in support of their NSPS requirement of 'no discharge' from refineries into the waters of the United States. Such ponds may provide a short-term method for the ultimate disposal of residual wastewaters in those locations where the soil's permeability and the sub-surface hydrology are suitable, or where the ponds are provided with liners or barriers to prevent wastewater pollutants from permeating to sub-surface aquifers. However, in the long-term, those ponds will eventually fill with accumulated, concentrated pollutants which must be removed and disposed of in a manner that secures them from dissolution in subsequent rainfall.

Research studies are needed to define the long-term problems of 'no discharge' or 'zero discharge'. The ultimate disposal of wastewater pollutants in evaporation-percolation ponds and in disposal wells does, in fact, constitute 'no discharge' into waters of the United States over the short-term. However, there remain the problems of protecting underground aquifers from long-term contamination and the problems of long-term disposal of the concentrated pollutants accumulated in the evaporation-percolation ponds. Studies of those problems should include a realistic assessment of the magnitude of improvements in the quality of the nation's waters to be expected from the refinery NSPS 'no discharge' requirement, and whether that requirement can be justified on a cost-benefit basis relative to control of other sources such as non-point sources[225].

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